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**(54) Color photographs and method for preparation of the same.**

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**EP-A- 0 145 342**  
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**PATENT ABSTRACTS OF JAPAN, vol. 3, no. 150 (E-158), 11th December 1979; & JP-A-54 130 928 (KONISHIROKU SHASHIN KOGYO K.K.) 10-11-1979**

**PATENT ABSTRACTS OF JAPAN, vol. 10, no. 210 (P-479)[2266], 23rd July 1986; & JP-A-61 50 136 (FUJI PHOTO FILM CO., LTD) 12-03-1986**

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**Description****FIELD OF THE INVENTION**

5 The present invention relates to color photographs and a method for preparation of the same, and more precisely, to color photographs and a method for preparation of color photographs having improved storability by chemically inactivating aromatic amine developing agents that exist in silver halide photographic materials after color development with storability improving agents.

**BACKGROUND OF THE INVENTION**

Silver halide color photographic materials are imagewise exposed and developed with an aromatic amine series color developing agent, and the resulting oxidation product of the developing agent is reacted with a color image-forming coupler (hereinafter referred to as "coupler") in the material to give color  
15 images. In color photographic materials, in general, combinations of a yellow coupler, a cyan coupler and a magenta coupler are used.

In 1912, Fisher, et al. discovered the fundamental of color development, and various improvements of the color development system have heretofore been noticeably effected. In particular, various improvements and studies have been extensively effected including, for example, shortening of development time,  
20 simplification of processing steps, re-use of waste solutions in development, reduction of the amount of replenishers, processing without water and removal of benzyl alcohol in consideration of preservation of the environment.

However, there still are many problems with conventional technical means. For instance, in actual development processing, a fresh processing solution is not used for each development procedure but the  
25 developer is replenished in accordance with the amount of the materials to be developed, and the replenishment of the developer causes some problems in the development procedure.

In general, a development processing solution comprises a color developer, a stop solution, a bleaching solution, a fixer or a blix and the processing temperature is high, being 31 °C to 43 °C. Accordingly, the developing agent is decomposed when used for a long period of time or is oxidized by contact with air, or  
30 some components in the photographic materials as processed are dissolved out and precipitate in the processing solution during the processing of the materials, or the processing solution sticks to the materials as processed and is carried over into the next bath together with the materials, whereby the composition of the processing solution will often vary. A processing solution thus run for a long period of time becomes a so-called running solution. Under such situations, replenishment of deficient chemical components is  
35 effected and removal of undesired components is also effected, but these treatments are not satisfactory. Further, in the rinsing step, the amount of the rinsing water to be used is desired to be reduced or the rinsing step is desired to be effected without water because of a shortage of water resources, rise in city water costs, and other economical and environmental reasons. In such water-free treatment, however, inorganic components such as thiosulfates, sulfites or meta-bisulfites present in the processing solution as  
40 well as organic components such as a developing agent present in the developer solution enter into or adhere onto the photographic materials processed.

Further, in view of the deterioration of the composition of the treating solution as it is used, the reduction of the amount of the rinsing water in the rinsing step and the water-free processing step, it is evident that the amount of the components of the processing solution which enter into or adhere onto the  
45 photographic materials processed tends to increase remarkably.

On the other hand, regarding couplers to be incorporated into photographic materials, development of couplers capable of forming sharp cyan, magenta or yellow dyes with less side-absorption is being effected so as to attain a good color reproduction, and at the same time, development of highly active couplers capable of being color-developed in a short period of time is also being effected. Further, development of  
50 new additives capable of effectively inducing the excellent characteristics of these couplers is also being effected. Unfortunately, however, the newly induced characteristics often cause deterioration of the storability of the color photographs due to the reaction with the components of the processing solution that remain in the photographic materials after being processed.

It is known that the components of the processing solution that remain in the photographic materials  
55 after development, especially the developing agent which is an aromatic primary amine compound and compounds derived therefrom, cause the deterioration of the fastness of the image formed, for example, because of the influence of light, heat, moisture, oxygen, during storage for a long period of time, or the compounds themselves self-couple or convert into colored substances by the action of any co-existing

materials to form so-called "stains". This is a fatal defect in color photographs.

On the other hand, various studies have been made relating to the prevention of image deterioration and stain prevention, apart from the above-mentioned technical means. For instance, various technical ideas have been proposed, including the selective use of hardly color-fading couplers, the use of an anti-fading agent for preventing the color images formed from fading under light, and the use of an ultraviolet absorbent for preventing the color images formed from being deteriorated by ultraviolet rays.

In particular, the effect of preventing image deterioration by the use of an anti-fading agent is remarkable, and for example, hydroquinones, hindered phenols, tocopherols, chromans, coumarans and compounds derived from these compounds by etherifying the phenolic hydroxyl group therein (U.S. Patent 3,935,016, 3,930,866, 3,700,455, 3,764,337, 3,432,300, 3,573,050 and 4,254,216, British Patents 2,066,975 and 1,326,889 and Japanese Patent Publication No. 30462/76), are known as anti-fading agents.

However, these compounds are still insufficient to provide images of high quality, although the compounds are accepted as having the effect of anti-fading agents for preventing the fading or discoloration of image dyes formed. In addition, these compounds often cause variation in the hue of color images, generation of fog, occurrence of dispersion insufficiency or even formation of fine crystals in coated emulsions, and therefore, these compounds cannot be said to be able to display all-around effect for photographic use.

Recently certain kinds of amine series compounds have been proposed to be effective for the prevention of stains, for example, U.S. Patent 4,463,085 and 4,483,918, Japanese Patent Application (OPI) Nos. 218445/84 and 229557/84, (the term "OPI" as used herein refers to a "published unexamined Japanese patent application"). However, none of these conventional compounds has been sufficient for attaining the object.

On the other hand, it is known to add a l-aryl-3-pyrazolidone derivative, especially a precursor thereof, to layers of photographic materials, for example, in U.S. Patents 4,358,525, 4,465,762 and 4,552,917, Japanese Patent Application (OPI) Nos. 52055/80, 5330/80, 40245/82, 104641/82 and 121328/84, However, these compounds have, when added, the defect of deteriorating the light-fastness of the photographic materials, and especially, the color-faded degree of remarkable for 3-alkoxycarbonyloxy-2-pyrazolidone derivatives.

### 30 SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a method for preparation of color photographs whose white background parts do not fade even when stored or placed on exhibition for along period of time.

Another object of the present invention is to provide color photographic materials capable of forming color images, after being color developed, bleached and fixed, which do not deteriorate or fade by the color developing agent that remains in the photographic material.

Still another object of the present invention is to provide a method for forming color images in color photographic materials, which are free from any harmful side-effects, such as image deterioration or stain generation, caused by aromatic amine color developing agents that remain in the photographic materials, even when the photographic materials are processed with processing solutions from which a noticeable amount of components of the processing solutions would enter into or adhere onto the photographic materials processed, such as processing solutions under a running state, rinsing solutions containing a small amount of water or water-free solutions, substantially benzyl alcohol-free color developers, or other processing solutions which would be a burden on color development.

The present inventors repeatedly studied various matters and as a result have found that the above-mentioned objects can effectively be attained by incorporating a storability-improving compound into a color photograph to be obtained by imagewise exposure, color development and bleaching and fixation of a color photographic material which contains a color image-forming coupler capable of forming a dye by an oxidation-coupling reaction of the silver halide emulsion layer as coated on the support of the material and an aromatic amine series color developing agent, in any stage of during the production of the photographic material, or during or after the color development, the storability-improving compound being able to form a chemical bond with the aromatic amine series developing agent to give a chemically inactive and substantially colorless compound.

The present invention was achieved on the basis of the above-described discovery.

Specifically, the subject matter of the present invention resides in a color photograph which contains a storability-improving compound capable of forming a chemical bond with an aromatic amine series color developing agent under the condition of a pH of 8 or less that remains in the photograph after the color

development thereof, to give a chemically inactive and substantially colorless compound, in at least one photographic layer on the support of the photograph.

#### DETAILED DESCRIPTION OF THE INVENTION

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The aromatic amine series color developing agents as referred to herein include aromatic primary, secondary and tertiary amine compounds, and more precisely, there may be mentioned phenylenediamine series compound and aminophenol series compounds. Typical examples of these compounds are 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline, 4-methyl-2-amino-N,N-diethylaniline, 4-methyl-2-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 2-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-methylamino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-dimethylamino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-butylamino-N,N-diethylaniline, 3-methyl-4-acetylamino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-methanesulfonamido-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-benzylamino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-cyclohexylamino-N-ethyl-N-methylaniline and their sulfates, hydrochlorides, phosphates, p-toluenesulfonates, tetraphenylborates and p-(t-octyl)benzenesulfonates, as well as o-aminophenol, p-aminophenol, 4-amino-2-methylphenol, 2-amino-3-methylphenol and 2-hydroxy-3-amino-1,4-dimethylbenzene.

In addition, the compounds described in L.F.A. Mason's *Photographic Processing Chemistry* (by Focal Press), pages 226-229 (1966), U.S. Patents 2,193,015 and 2,592,364, Japanese Patent Application (OPI) No. 64933/73 can also be used.

The compounds capable of forming a chemical bond with the aromatic amine series color developing agent after color development to give a chemically inactive and substantially colorless compound are those represented by the following general formulae (I) and (II):

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In the formulae,  $R_1$  and  $R_2$  each represents an aliphatic group, an aromatic group or a heterocyclic group; X represents a group capable of reacting with an aromatic amine developing agent to be removed; A represents a group capable of reacting with an aromatic amine developing agent to form a chemical bond; n represents 1 or 0; B represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group or a sulfonyl group; Y represents a group capable of accelerating the addition of an aromatic amine developing agent to the compound of the formula (II); and  $R_1$  and X, and Y and  $R_2$  or B may be bonded together to form a cyclic structure (e.g., a cyclic acid anhydride, a succinimido ring).

In the reaction for forming a chemical bond with the remaining aromatic amine developing agent a substitution reaction and an addition reaction are typical reactions.

Among the compounds of the formulae (I) and (II) capable of reacting with the remaining aromatic amine series color developing agent, those of the formula (I) are preferred, more preferably compounds capable of reacting at a secondary reaction rate constant  $k_2$  (80°C) with p-anisidine of from 1.0 liter/mol·sec. to  $1 \times 10^{-5}$  liter/mol·sec, most preferably compounds capable of reacting at a secondary reaction rate constant  $k_2$  (80°C) with p-anisidine of from  $1 \times 10^{-1}$  liter/mol·sec to  $1 \times 10^{-4}$  liter/mol·sec.

If the constant  $k_2$  is larger than 1.0 liter/mol·sec., the compounds themselves are unstable and easy to react with gelatin or water to decompose. On the other hand, if the constant  $k_2$  is smaller than  $1 \times 10^{-5}$  liter/mol·sec., the reaction rate in the reaction with the remaining aromatic amine developing agent is low, and as a result, the prevention of the side-effect of the remaining aromatic amine developing agent, which is the object of the present invention, tends to be reduced.

The method for measurement of the constant  $k_2$  is explained in the examples to follow hereinafter. The substituents in the compounds of the formulae (I) and (II) are explained in greater detail below.

The aliphatic group represented by  $R_1$ ,  $R_2$  and B means a linear, branched or cyclic alkyl, alkenyl or

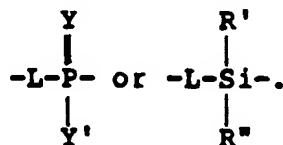
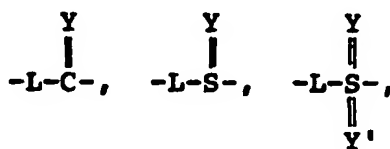


alkynyl group, which may optionally be substituted by substituent(s). The aromatic group represented by  $R_1$ ,  $R_2$  and B means either of a carbon-cyclic aromatic group (such as a phenyl group, a naphthyl group,) and a heterocyclic aromatic group (such as a furyl group, a thienyl group, a pyrazolyl group, a pyridyl group, an indolyl group,), which may be either a mono-cyclic system or a condensed cyclic system (such as a benzofuryl group, a phenanthridinyl group,). Further these aromatic rings can optionally have substituent(s).

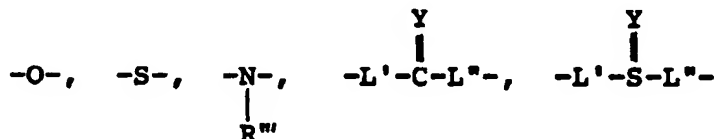
The heterocyclic group represented by  $R_1$ ,  $R_2$  and B is preferably a group having a 3-membered to 10-membered cyclic structure which is composed of carbon, oxygen, nitrogen, sulfur and/or hydrogen atoms, and the hetero-ring itself may be a saturated ring or an unsaturated ring and may further be substituted by substituent(s) (for example, a coumarinyl group, a pyrrolidyl group, a pyrrolinyl group, a morpholinyl group,).

X represents a group capable of reacting with an aromatic amine developer to be removed and is preferably a group linked with A via an oxygen atom, a sulfur atom or a nitrogen atom (such as a 3-pyrazolyloxy group, a 3H-1,2,4-oxadiazolin-5-oxogroup, an aryloxy group, an alkoxy group, an alkylthio group, an arylthio group, a substituted N-oxy group) or a halogen atom. When X is a halogen atom, n is 0.

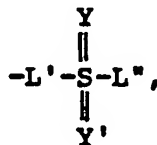
A represents a group capable of reacting with an aromatic amine developing agent to form a chemical bond and is, for example, a group containing a low electron density atom. This includes, for example,



In these groups, L represents a single bond, an alkylene group,



or



for example, a carbonyl group, a sulfonyl group, a sulfinyl group, a hydroxycarbonyl group, a phosphonyl group, a thiocarbonyl group, an aminocarbonyl group, a silyloxy group.

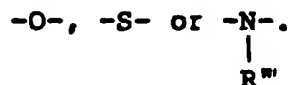
Y has the same meaning as Y in the formula (II), and Y' has the same meaning as Y.

$R'$  and  $R''$  may be the same or different and each represents  $-\text{L}''-\text{R}_0$ .

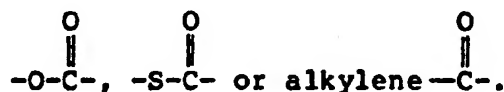
$R_0$  has the same meaning as  $R_1$ .  $R''$  represents a hydrogen atom, an aliphatic group (such as a methyl group, an isobutyl group, a t-butyl group, a vinyl group, a benzyl group, an octadecyl group, a cyclohexyl group,), an aromatic group (such as a phenyl group, a pyridyl group, a naphthyl group,), a heterocyclic

group (such as a piperidiny group, a pyranly group, a furanyl group, a chromanyl group,), an acyl group (such as an acetyl group, a benzoyl group,) or a sulfonyl group (such as a methanesulfonyl group, a benzenesulfonyl group,).

L', L" and L''' each represents

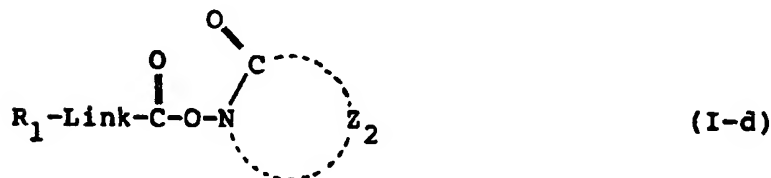
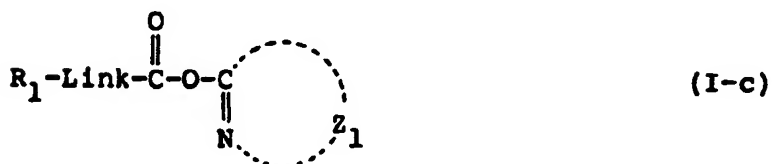


In particular, A is preferably a divalent group as represented by



The storability-improving compound used in the present invention is different from the 3-alkoxycarbonyloxy-2-pyrazolidone derivative such as a development accelerator.

More preferable examples of the compound represented by the general formula (I) are those represented by the following general formulae (I-a), (I-b), (I-c) and (I-d) and which react with p-anisidine at a secondary reaction rate constant  $k_2$  (80°C) within the range of  $1 \times 10^{-1}$  liter/mol\*sec to  $1 \times 10^{-5}$  liter/mol\*sec:



where  $R_1$  has the same meaning as  $R_1$  in formula (I); Link is a single bond or -O-; Ar denotes an aromatic group having the same meaning as defined for  $R_1$ ,  $R_2$  and B, except that no group useful as a photographic reducing agent such as a hydroquinone derivative of a catechol derivative will be released as a result of reaction with an aromatic amine series developing agent; Ra, Rb and Rc which may be the same or  
 5 different each represents a hydrogen atom, or an aliphatic group, an aromatic group or a heterocyclic group having the same meaning as defined for  $R_1$ ,  $R_2$  and B; Ra, Rb and Rc may further represent an alkoxy group, an aryloxy group, a heterocyclic oxy group, an alkylthio group, an arylthio group, a heterocyclic thio group, an amino group, an alkylamino group, an acyl group, an amino group, a sulfonamido group, a sulfonyl group, an alkoxy carbonyl group, a sulfo group, a carboxyl group, a hydroxyl group, an acyloxy  
 10 group, a ureido group, a urethane group, a carbamoyl group or a sulfamoyl group, provided that Ra and Rb, or Rb and Rc, may combine to form a 5- to 7-membered hetero ring, which hetero ring may be further substituted by a substituent, or form a spiro ring or a bicyclo ring, or may be fused with an aromatic ring;  $Z_1$  and  $Z_2$  denotes the non-metallic atomic group necessary for forming a 5- to 7-membered hetero ring, which hetero ring may be further substituted by a substituent, or form a spiro ring or a bicyclo ring, or may  
 15 be fused with an aromatic ring, except that  $Z_1$  is not such a group that it will release a coupler, a 1-phenyl-3-pyrazolide as a result of reaction with an aromatic amine series developing agent.

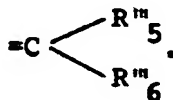
Compounds of formulae (I-a) to (I-d), in particular, compounds of formula (I-a), may be adjusted to have a secondary reaction rate  $k_2$  (80°C) with p-anisidine in the range of from  $1 \times 10^{-1}$  liter/mol·sec to  $1 \times 10^{-5}$  liter/mol·sec by selecting appropriate substituents if Ar is a carbon-ring based aromatic group.  
 20 Depending on the type of group denoted by  $R_1$ , the total of the Hammett's  $\sigma$  value of the individual substituents is preferably at least 0.2, more preferably at least 0.4, most preferably at least 0.6.

If compounds of formula (I-a) or (I-b) are added during the manufacture of light-sensitive materials, the total number of carbon atoms in the compounds per se is preferably at least 13, and the more the carbon atoms that are present, the better.

25 In order to attain the objects of the present invention, the compound of formula (I) is preferably such that it will not decompose during development or subsequent processing.

Y in the formula (II) is preferably an oxygen atom, a sulfur atom, =N-R<sup>4</sup>, or

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35 In the said groups,  $R^m_4$ ,  $R^m_5$  and  $R^m_6$  each represents a hydrogen atom, an aliphatic group (such as a methyl group, an isopropyl group, a t-butyl group, a vinyl group, a benzyl group, an octadecyl group, a cyclohexyl group.), an aromatic group (such as a phenyl group, pyridyl group, a naphthyl group.), a heterocyclic group (such as a piperidyl group, a pyranyl group, a furanyl group, a chromanyl group.), an acyl group (such as an acetyl group, a benzoyl group,) or a sulfonyl group (such as a methanesulfonyl  
 40 group, a benzenesulfonyl group.), and  $R^m_5$  and  $R^m_6$  may be bonded together to form a cyclic structure.

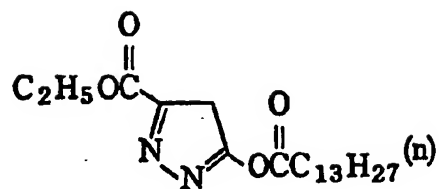
Typical examples of these compounds are set forth below, but the compounds for use in the present invention are not whatsoever limited by them.

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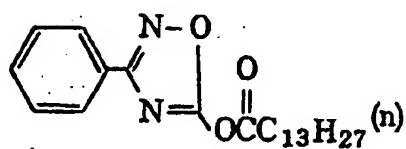
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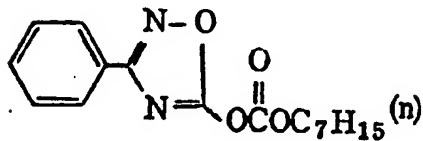
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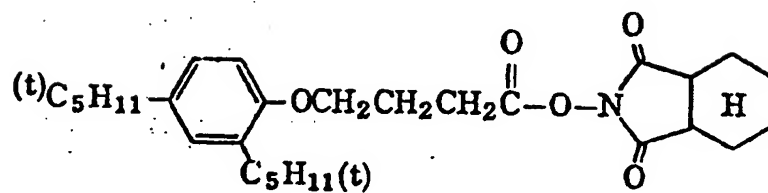
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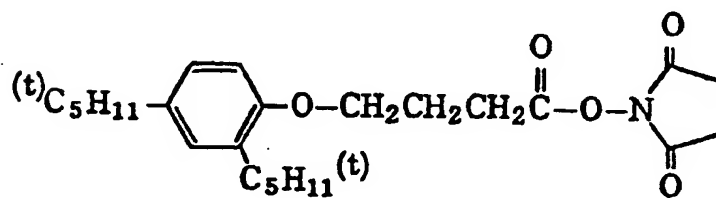
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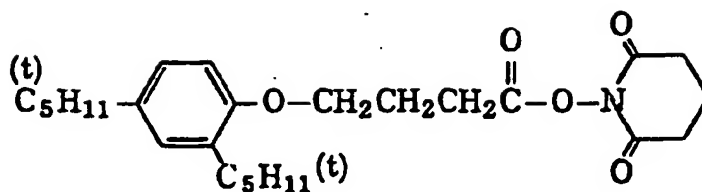
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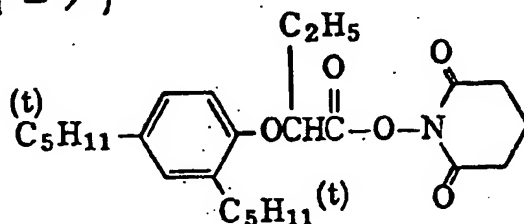
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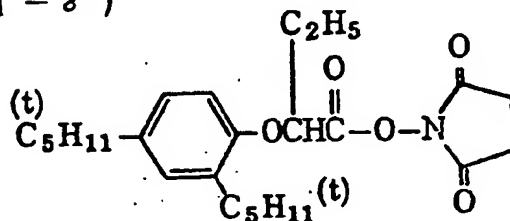
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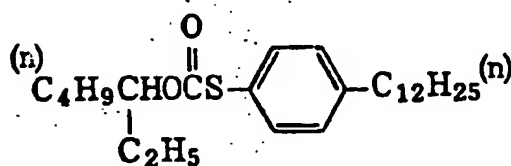
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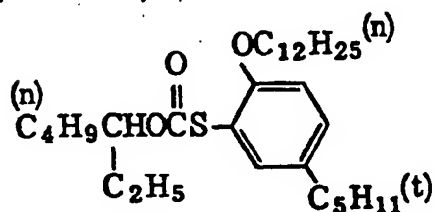
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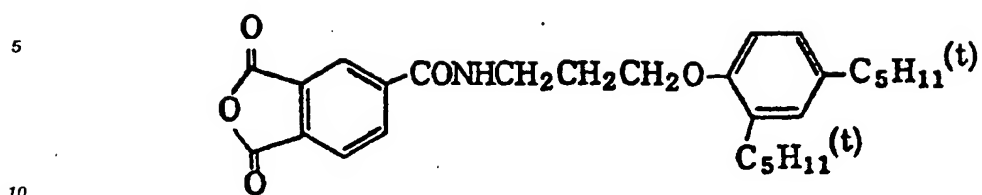
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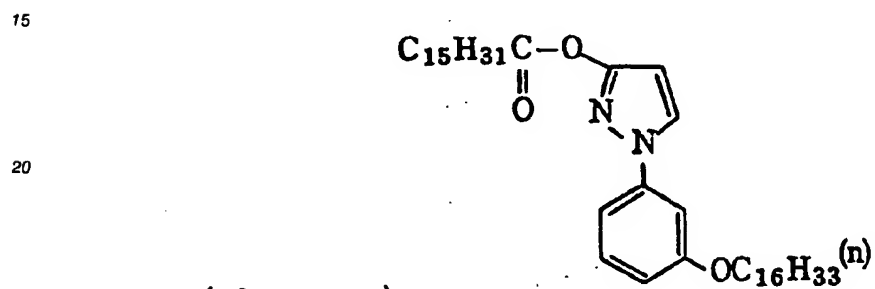
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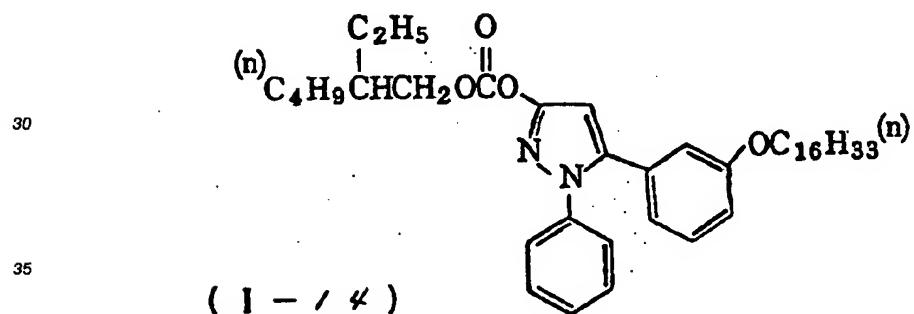
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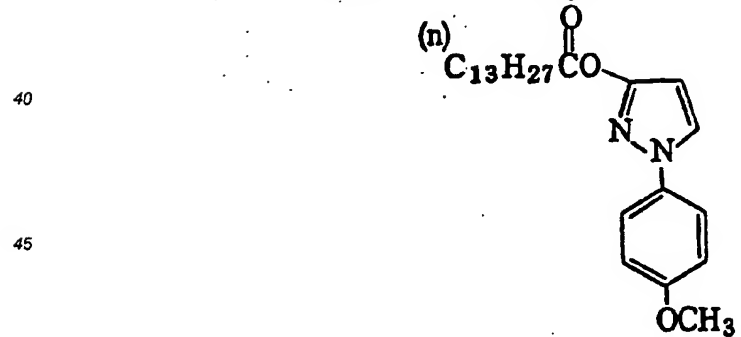
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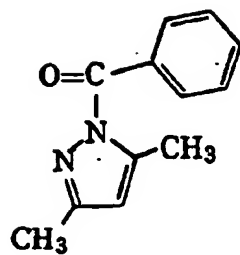
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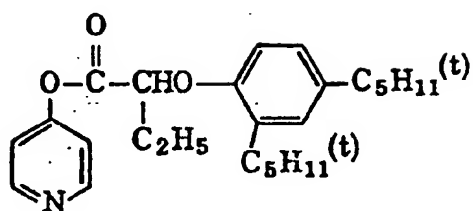
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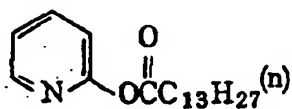
( I - / 5 )



( I - / 6 )



( I - / 7 )



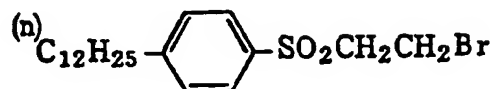
( I - / 8 )



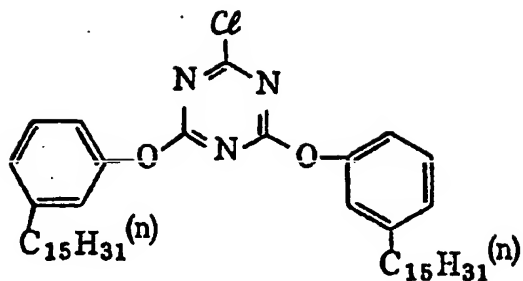
( I - / 9 )



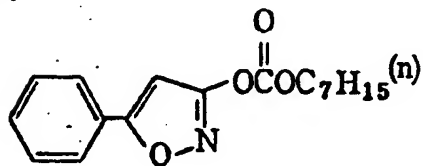
( I - 2 0 )



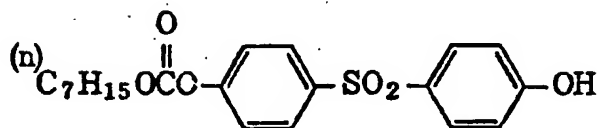
( I - 2 / )



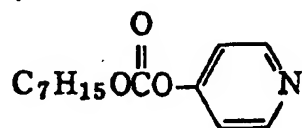
( I - 2 2 )



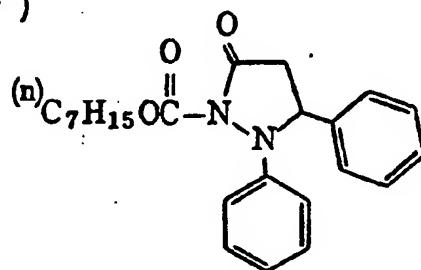
( I - 2 3 )



( I - 2 4 )

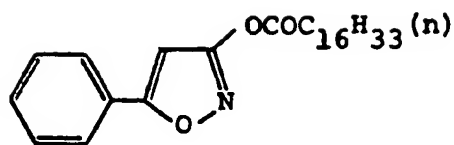


( I - 2 5 )

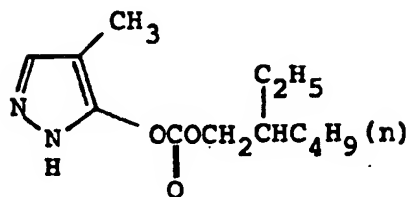




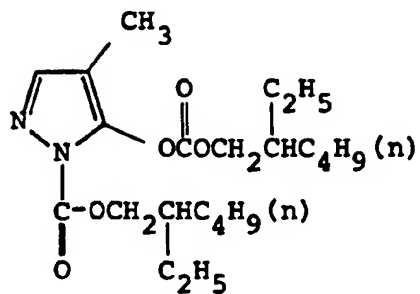
(I-26)



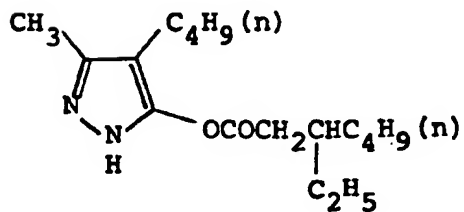
(I-27)



(I-28)



(I-29)

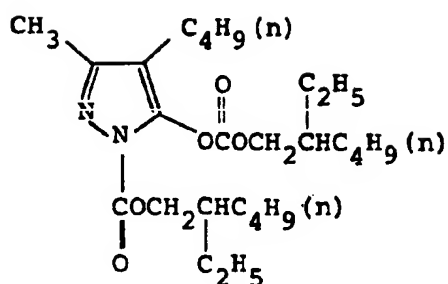


(I-30)

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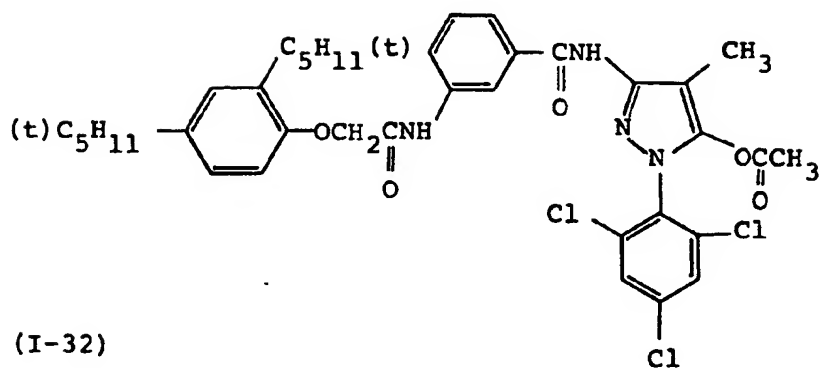


(I-31)

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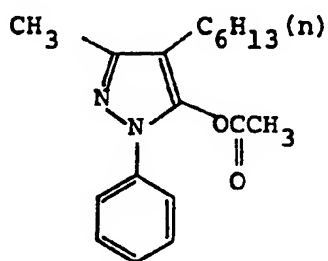
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(I-32)

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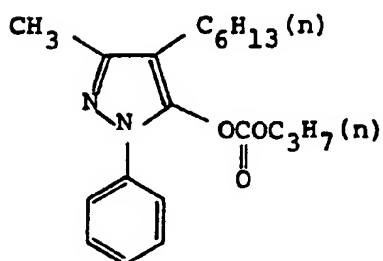
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(I-33)

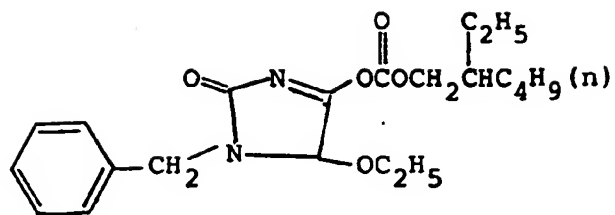
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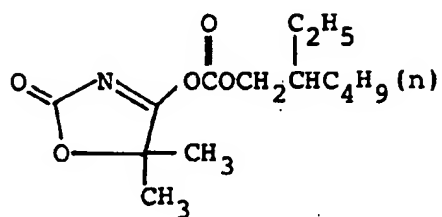


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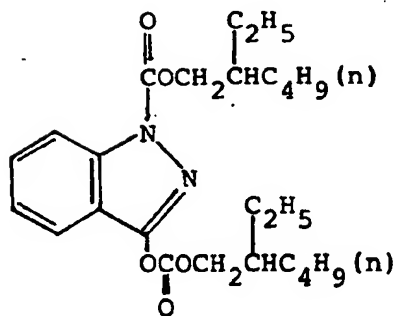
(I-34)



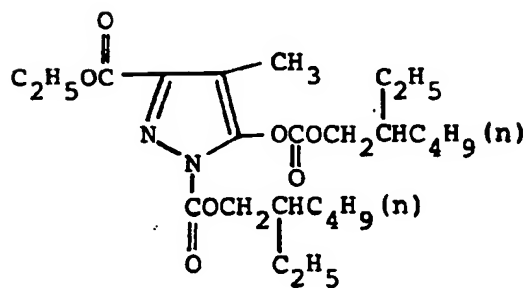
(I-35)



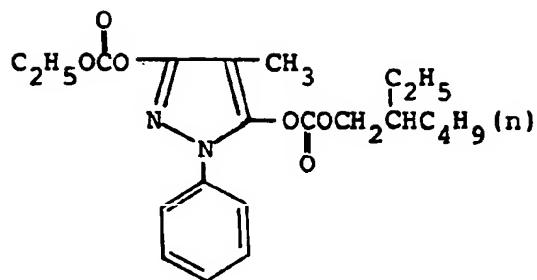
(I-36)



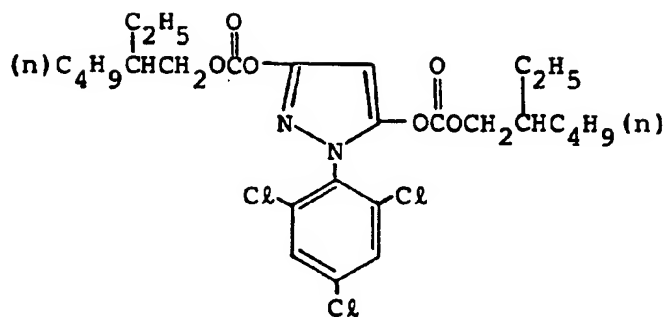
(I-37)



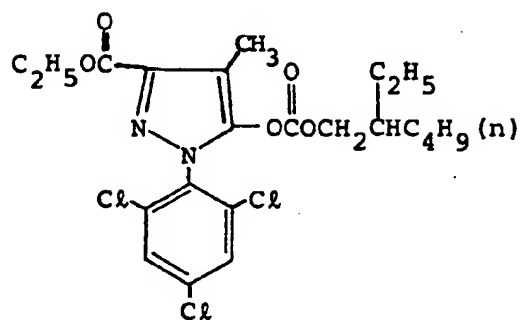
(I-38)



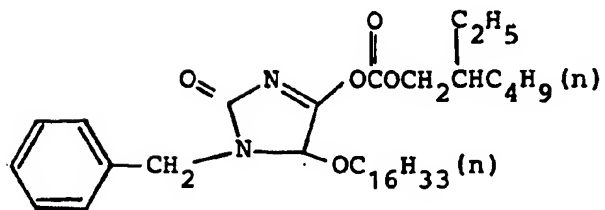
(I-39)



(I-40)

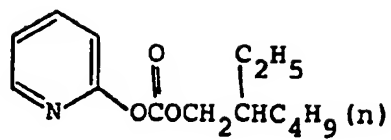


(I-41)



(I-42)

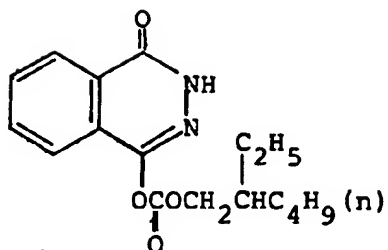
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(I-43)

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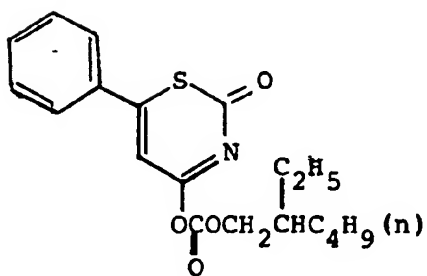


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(I-44)

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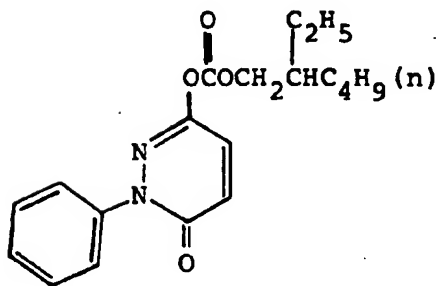


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(I-45)

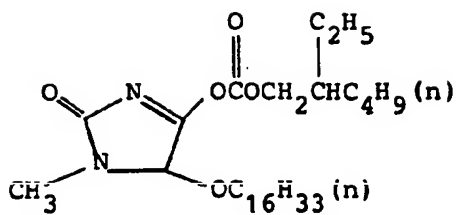
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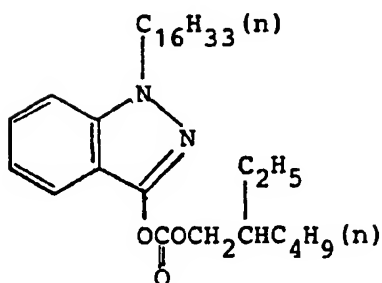
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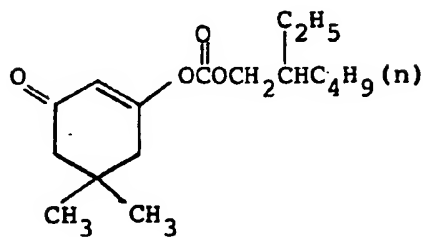
(I-46)



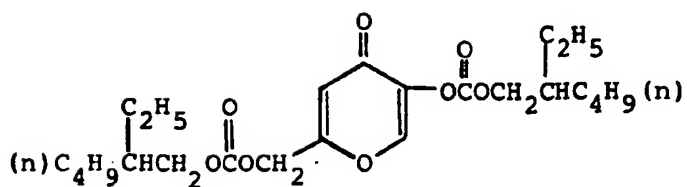
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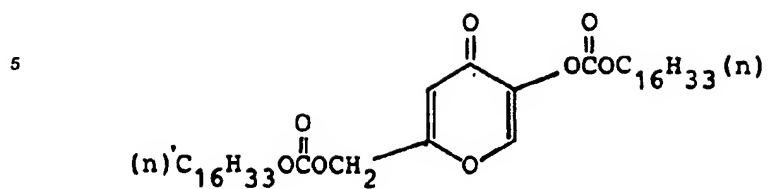
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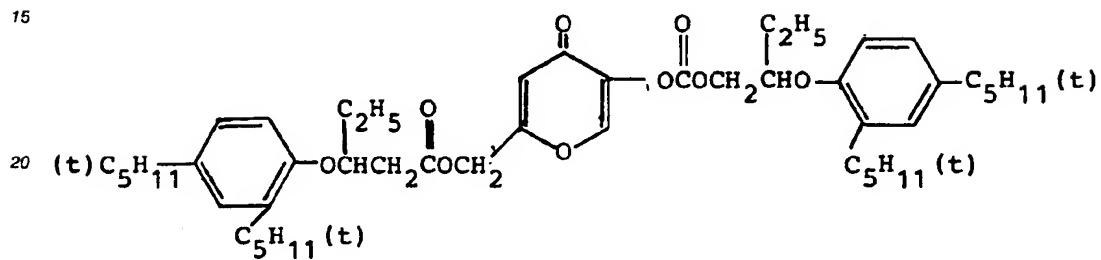
(I-49)



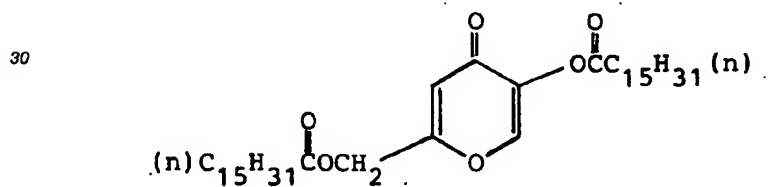
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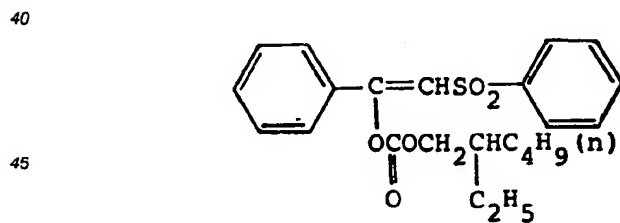
(I-51)



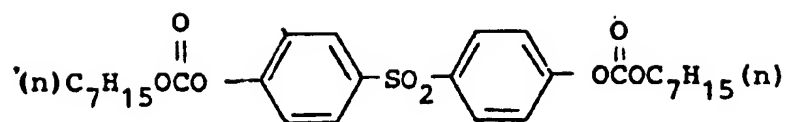
(I-52)



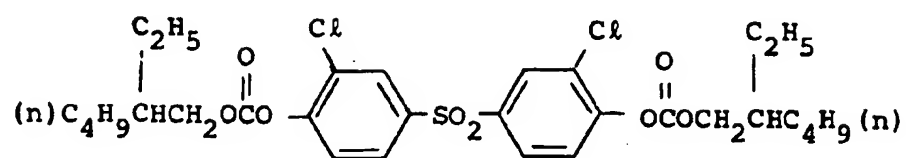
(I-53)



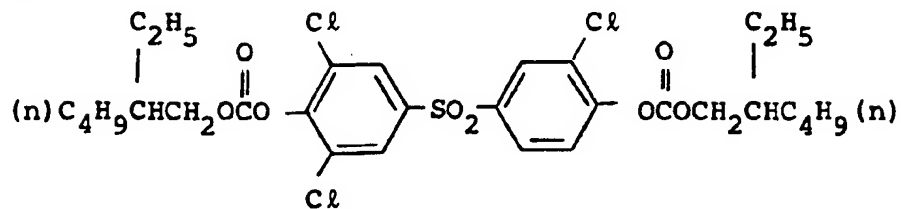
(I-54)



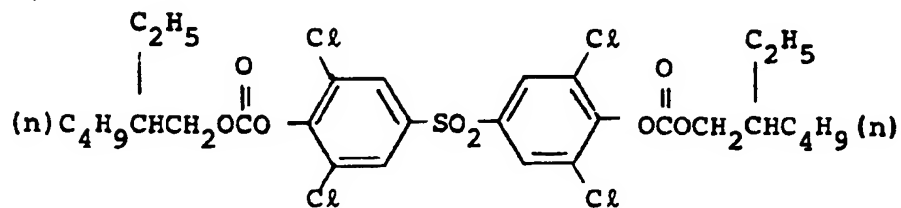
(I-55)



(I-56)

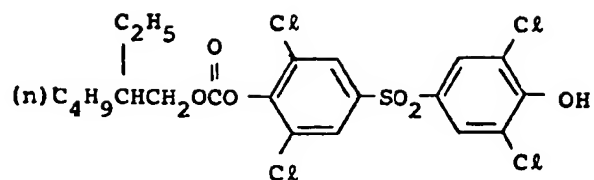


(I-57)

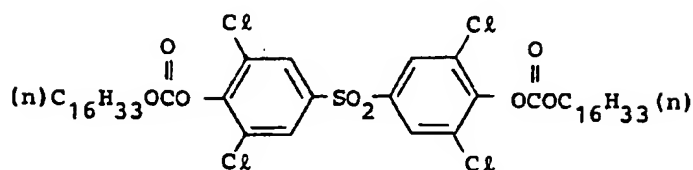




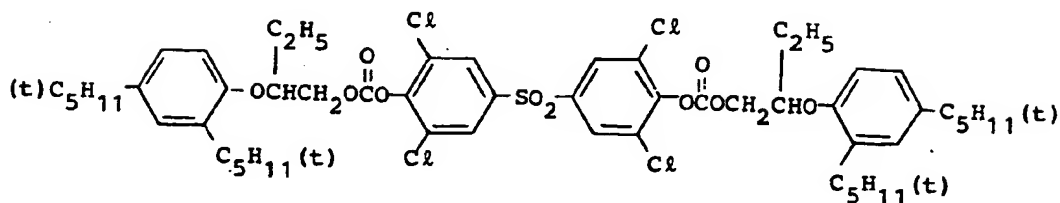
(I-58)



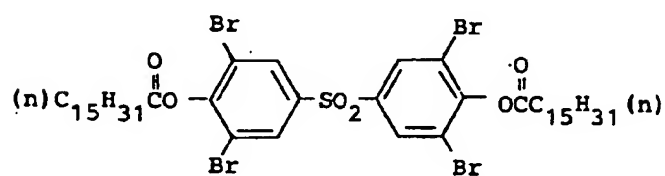
(I-59)



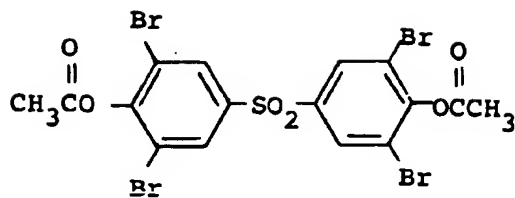
(I-60)



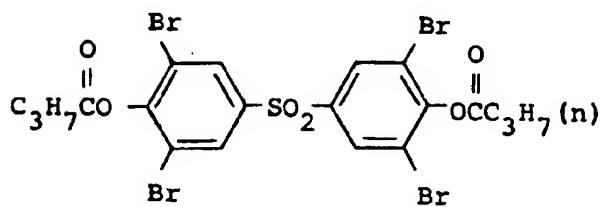
(I-61)



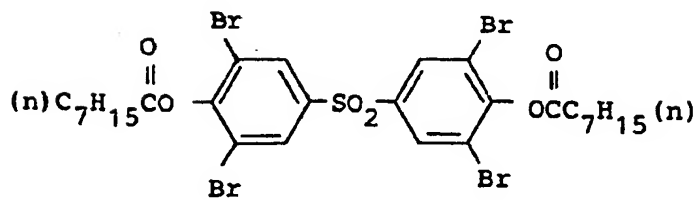
(I-62)



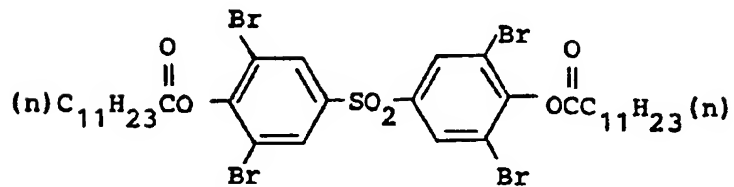
(I-63)



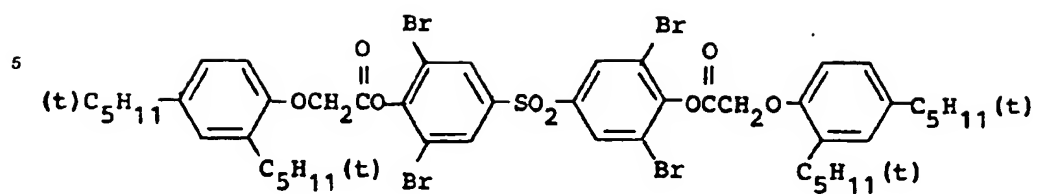
(I-64)



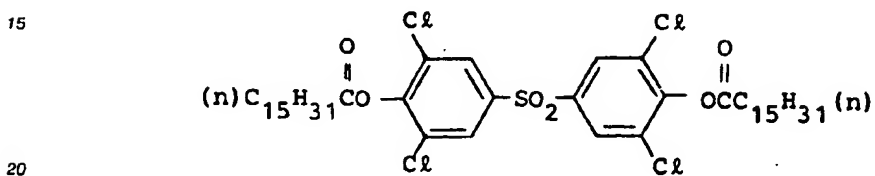
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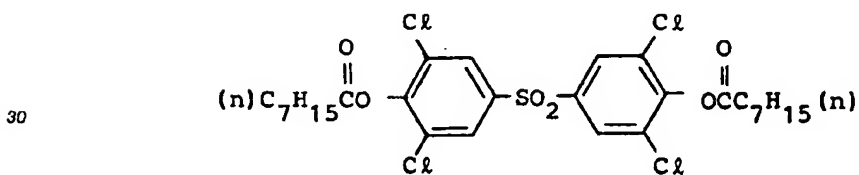
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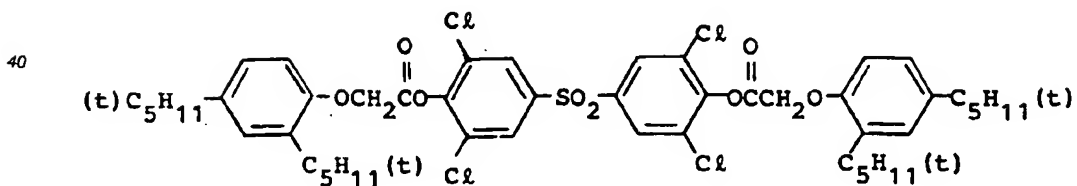
(I-67)



(I-68)

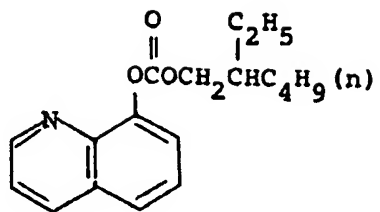


(I-69)



(I-70)

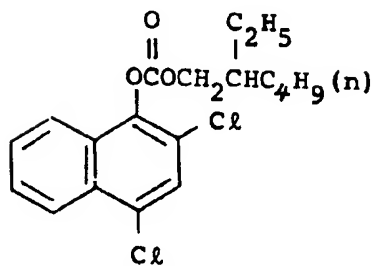
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(I-71)

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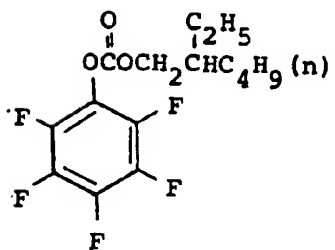


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(I-72)

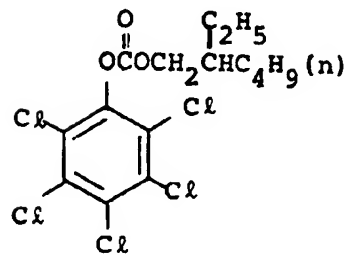
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(I-73)

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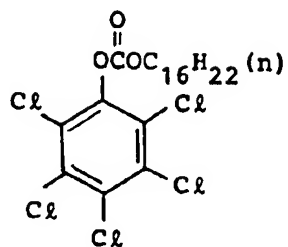
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(I-74)

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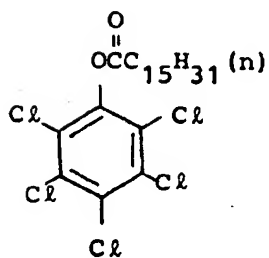
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(I-75)

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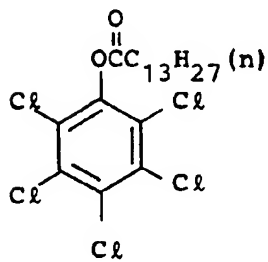
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(I-76)

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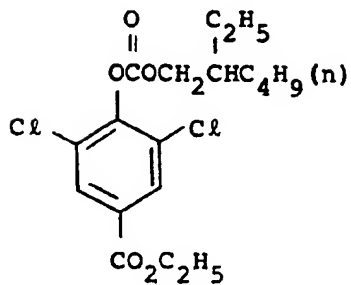


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(I-77)

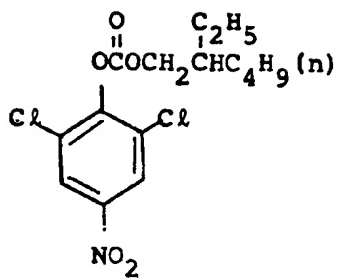
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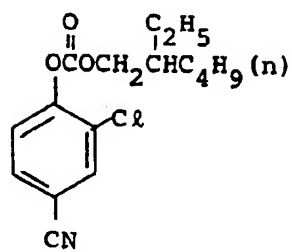


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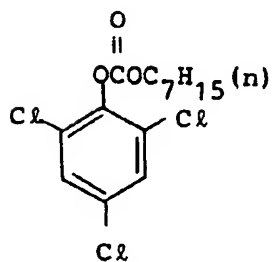
(I-78)



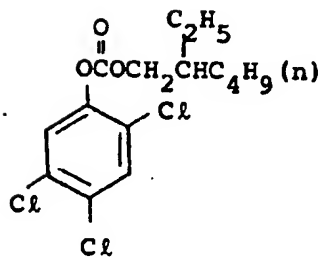
(I-79)



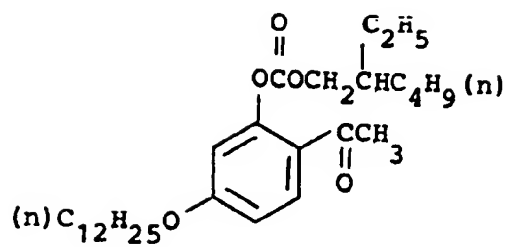
(I-80)



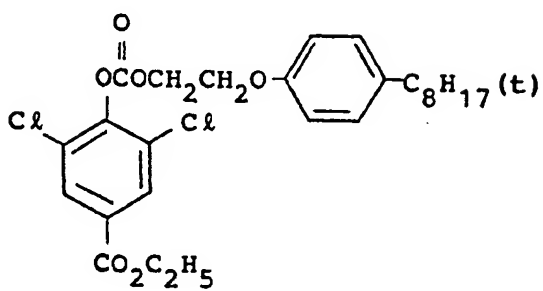
(I-81)



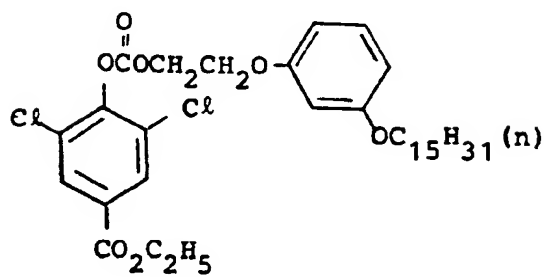
(I-82)



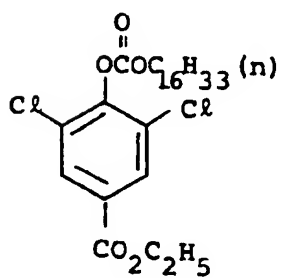
(I-83)



(I-84)



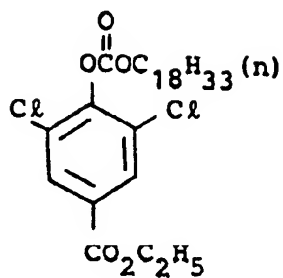
(I-85)



(I-86)

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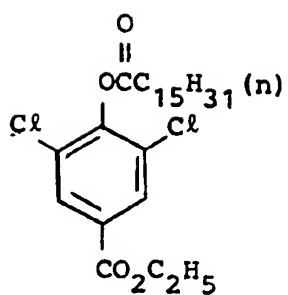


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(I-87)

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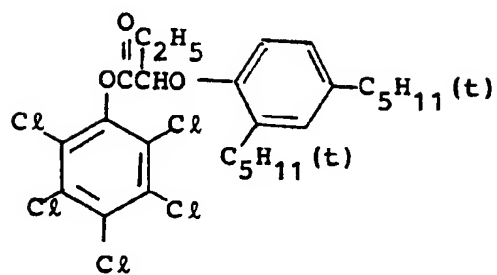


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(I-88)

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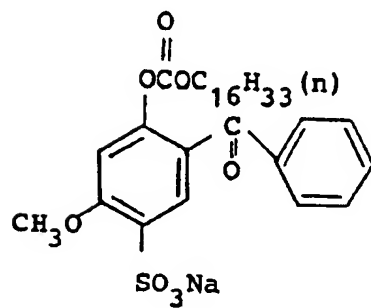


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(I-89)

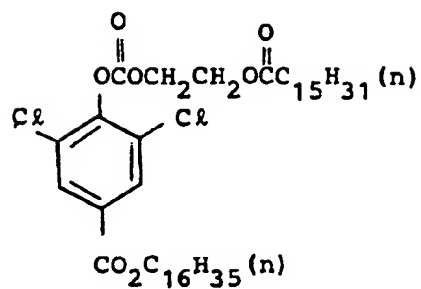
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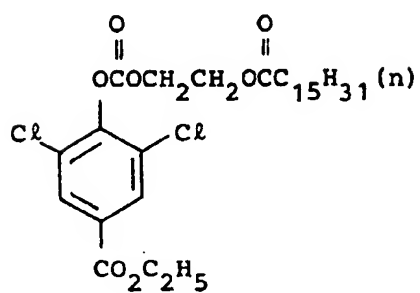




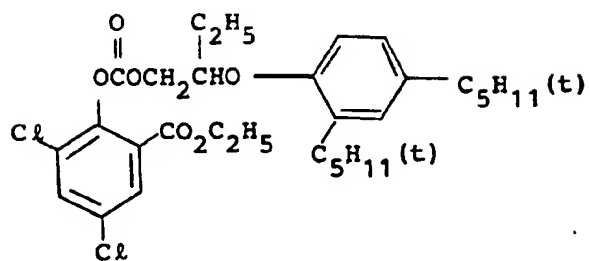
(I-90)



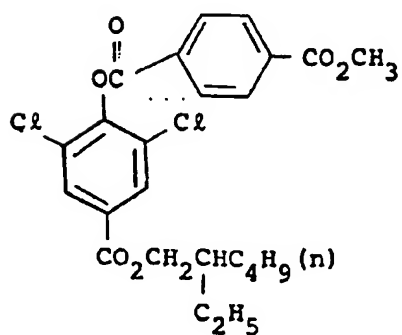
(I-91)



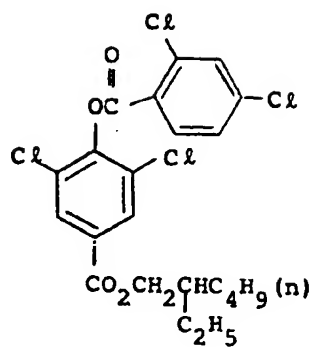
(I-92)



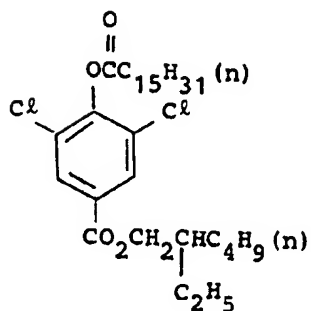
(I-93)



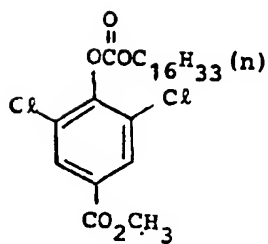
(I-94)



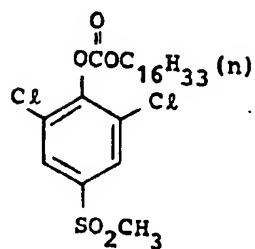
(I-95)



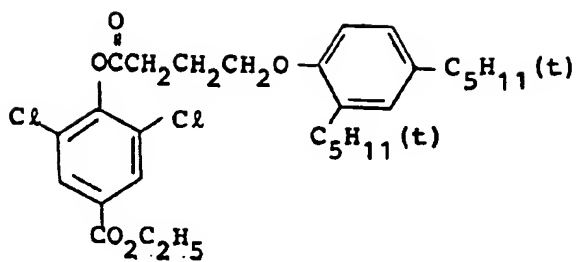
(I-96)



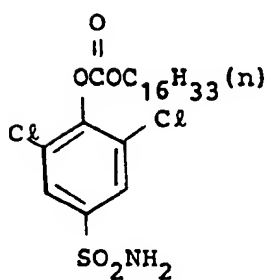
(I-97)



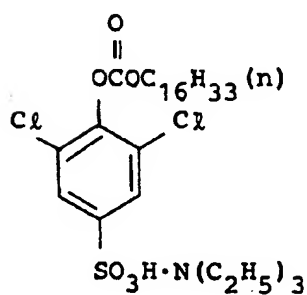
(I-98)



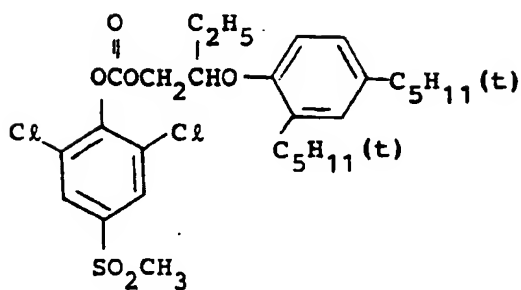
(I-99)



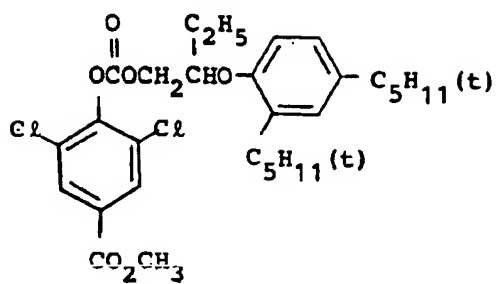
(I-100)



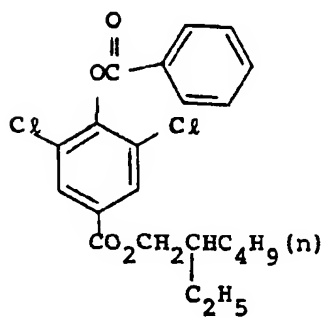
(I-101)



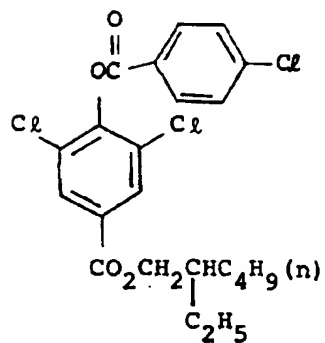
(I-102)



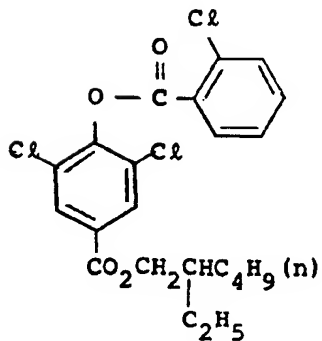
(I-103)



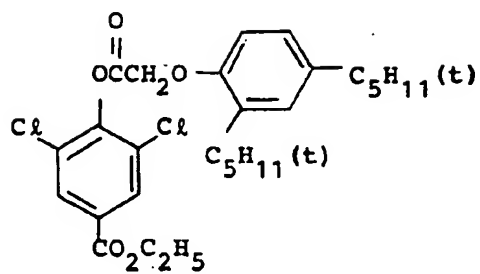
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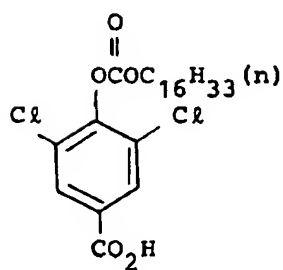
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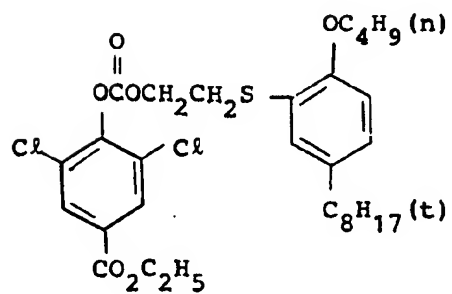
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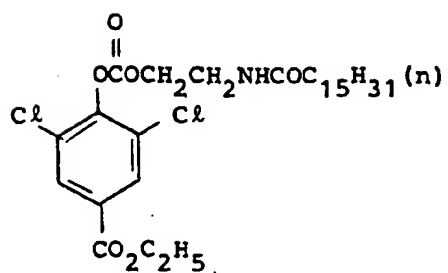
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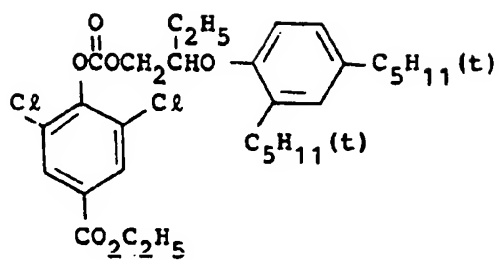
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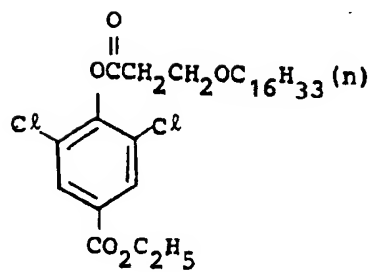
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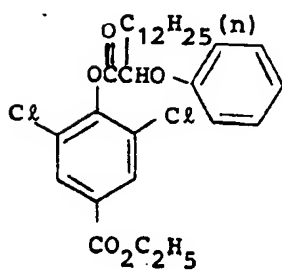
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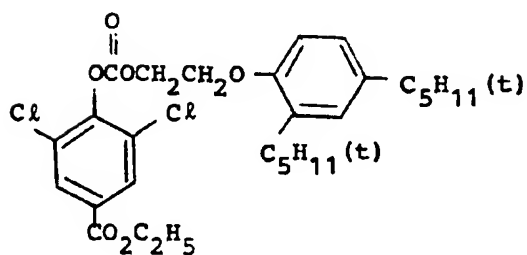
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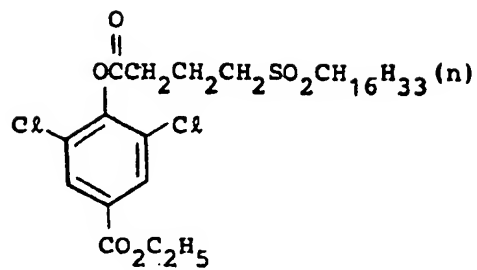
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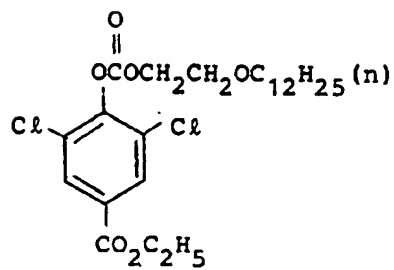
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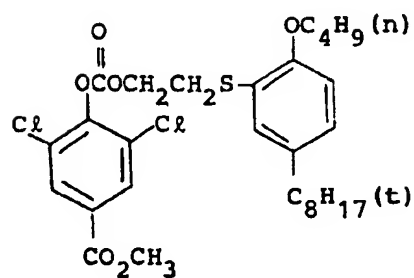
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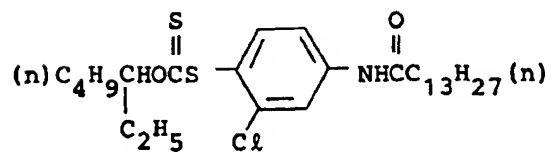
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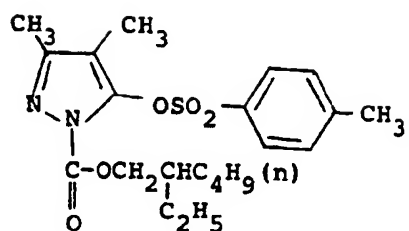
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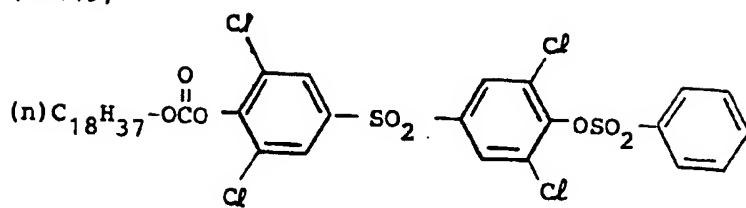
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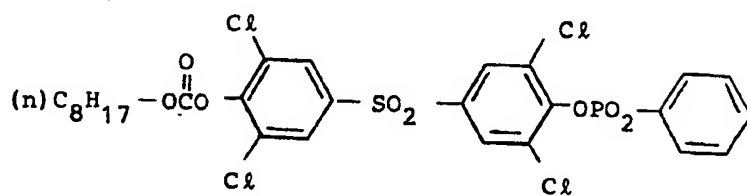
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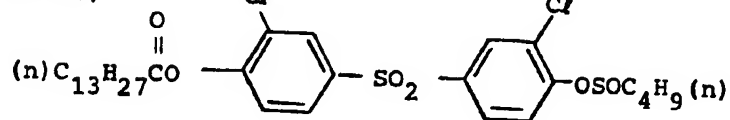
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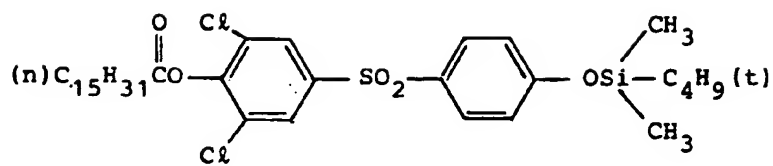


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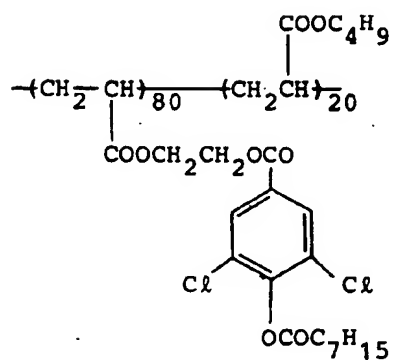




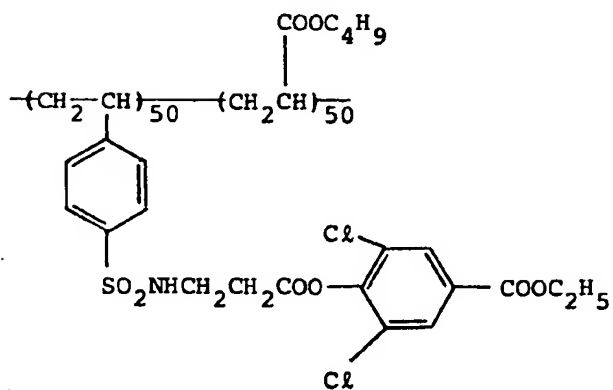
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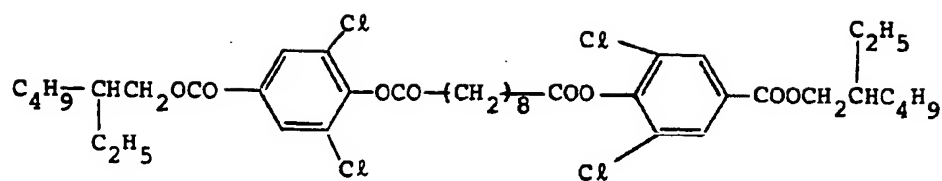
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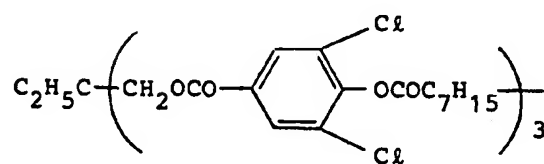
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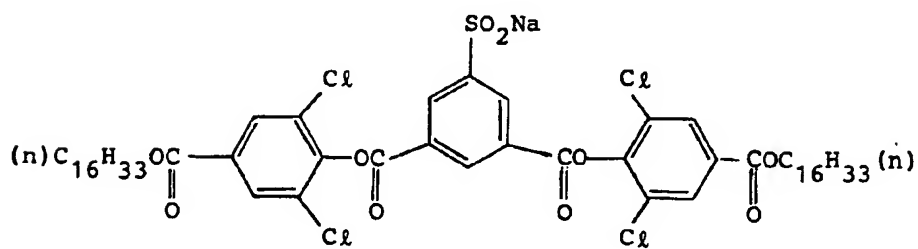
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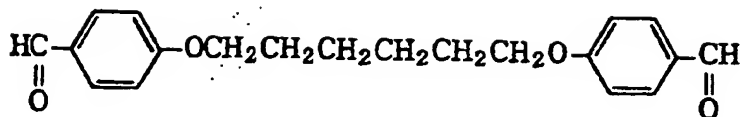
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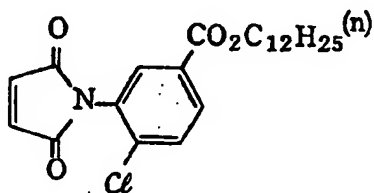
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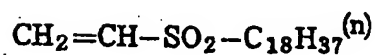
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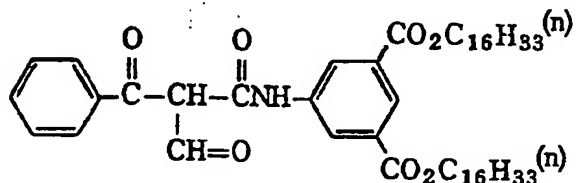
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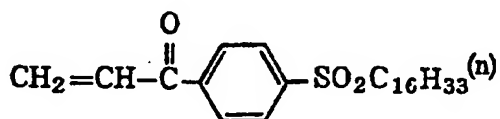
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( II - 4 )



( II - 5 )



These storability-improving compounds used in the present invention can be synthesized by the known methods as described, for example, in E. Müller, Houben-Weyl Methoden Der Organischen Chemie, Georg Thieme Verlag, Stuttgart, Band VII and IX.

Examples of synthesis of typical compounds used in the present invention are set forth below.

#### SYNTHESIS EXAMPLE 1 (Synthesis of Compound I-9):

Synthesis of 2-ethylhexyl-4-dodecylbenzenethiocarbonate (above-mentioned Compound I-9):

150 ml of chloroform and 9.9 mol (0.071 mol) of triethylamine were added and dissolved in 18 g (0.065 mol) of 4-dodecylbenzenethiol and stirred at 25°C. To this was dropwise added 13.3 g (0.068 mol) of 2-ethylhexyl chlorocarbonate. After stirring for 30 minutes, a cold aqueous hydrochloric acid solution was added to the reaction mixture for liquid separation, and the chloroform layer separated was washed three times with cold water and dried with Glauber's salt. After the Glauber's salt was filtrated out, the chloroform was distilled out and the remaining precipitate was purified by column chromatography. The product was oily. Yield: 17.2 g, 61.2%.

Result of elementary analysis (C <sub>27</sub> H <sub>46</sub> O <sub>2</sub> S <sub>2</sub> )			
	C	H	S
Measured data (%)	74.34	10.66	14.91
Calculated data (%)	74.60	10.67	14.75

#### SYNTHESIS EXAMPLE 2 (Synthesis of Compound I-13):

##### (i) Synthesis of 5-(3-hexadecyloxyphenyl)-3-hydroxy-1-phenylpyrazole:

60 ml of toluene and 10 g (0.12 mol) of manganese dioxide were added to 6.3 g (0.013 mol) of 4,5-dihydroxy-5-(3-hexadecyloxyphenyl)-3-hydroxy-1-phenylpyrazole and, heated and stirred for 2 hours on a steam bath. After inorganic substances were filtrated out, the remaining filtrate was concentrated and dried to a solid, and the solid product was crystallized in 20 ml of ethyl acetate. The product crystallized had a melting point of from 108 to 109 °C. Yield: 5.8 g, 92.5%.

##### (ii) Synthesis of 3-(2-ethylhexyloxycarbonyloxy)-5-(3-hexadecyloxyphenyl)-1-phenyl-pyrazole (above-mentioned Compound I-13):

50 ml of chloroform and 1.9 ml (0.014 mol) of triethylamine were added and dissolved in 5.3 g (0.011 mol) of 5-(3-hexadecyloxyphenyl)-3-hydroxy-1-phenylpyrazole and stirred at 25 °C. To this was dropwise added 2.3 g (0.012 mol) of 2-ethylhexyl chlorocarbonate. After stirring for 30 minutes, cold water was added to the reaction mixture for liquid separation, and the chloroform layer separated was washed two times with 50 ml of cold water and then dried with Glauber's salt. After the Glauber's salt was filtrated out, the chloroform was distilled out, and the remaining precipitate was purified by column chromatography. The product was oily. Yield: 5.7 g, 82%.

Result of elementary analysis (C <sub>40</sub> H <sub>60</sub> N <sub>2</sub> O <sub>4</sub> )			
	C	H	N
Measured data (%)	76.13	9.47	4.11
Calculated data (%)	75.91	9.56	4.43

#### SYNTHESIS EXAMPLE 3 (Synthesis of Compound I-24):

##### 40 Synthesis of 4-heptyloxycarbonyloxy-pyridine (above-mentioned Compound I-24):

100 ml of chloroform and 7.3 ml (0.052 mol) of triethylamine were added and dissolved in 4.5 g (0.040 mol) of 4-hydroxypyridine-monohydrate and stirred at 25 °C. To this was dropwise added 8.9 g (0.050 mol) of heptyl chlorocarbonate. After stirring for 30 minutes, a cold aqueous hydrochloric acid solution was added to the reaction mixture for liquid separation, and the chloroform layer separated was washed two times with cold water and dried with Glauber's salt. After the Glauber's salt was filtrated out, the chloroform was distilled out and the remaining precipitate was purified by column chromatography and crystallized in ethanol. The product had a melting point of from 44 to 50 °C. Yield: 7.5 g, 83%.

Result of elementary analysis (C <sub>13</sub> H <sub>19</sub> NO <sub>3</sub> )			
	C	H	N
Measured data (%)	69.52	8.47	6.03
Calculated data (%)	69.31	8.50	6.22

#### SYNTHESIS EXAMPLE 4 (Synthesis of Compound I-57):

# EP 0 258 662 B1

Acetonitrile (150 ml) was added to 19.4 g of 3,3',5,5'-tetrachloro-4,4'-dihydroxybiphenylsulfone and 16.8 g of triethylamine with stirring. To the mixture, 21.2 g of 2-ethylhexyl chloroformate was added dropwise at room temperature. After continued stirring for 3 hours, extraction was conducted with ethyl acetate and the ethyl acetate layer was washed with water and dried. The concentrated ethyl acetate layer was purified by chromatography on silica gel column to obtain a white crystal of Compound I-57. Yield: 20.5 g, 58.4%. Melting point: 65 - 66 °C.

Result of elementary analysis (C <sub>30</sub> H <sub>38</sub> Cl <sub>4</sub> O <sub>3</sub> S)				
	C	H	Cl	S
Measured data (%)	51.41	5.47	20.21	4.61
Calculated data (%)	51.44	5.47	20.24	4.58

## SYNTHESIS EXAMPLE 5 (Synthesis of Compound I-61):

Acetonitrile (300 ml) was added to 11.3 g of 3,3',5,5'-tetrabromobiphenylsulfone and 6.1 ml of triethylamine with stirring. To the mixture, 12.3 g of palmitic acid chloride was added dropwise at room temperature. After continued stirring for 5 hours, the reaction mixture was poured into 500 ml of water. The resulting crystal was recovered by filtration, washed with water and dried. Recrystallization with a mixed solvent of chloroform and ethyl acetate produced a crystal of Compound I-61. Yield: 17.5 g, 84.0%. Melting point: 125 - 126 °C.

Result of elementary analysis (C <sub>44</sub> H <sub>66</sub> Br <sub>4</sub> O <sub>3</sub> S)				
	C	B	Br	S
Measured data (%)	50.60	6.21	30.39	3.11
Calculated data (%)	50.68	6.38	30.66	3.07

## SYNTHESIS EXAMPLE 6 (Synthesis of Compound I-67):

Acetonitrile (300 ml) was added to 14.0 g of 3,3',5,5'-chloro-4,4'-dihydroxybiphenylsulfone and 11.2 ml of triethylamine with stirring. To the mixture, 22.0 g of palmitic acid chloride was added dropwise at room temperature. After completion of the addition, the internal temperature of the reaction system was elevated to 65 to 70 °C and the mixture was stirred for 1 hour. After completion of the reaction, the reaction mixture was poured into 1,000 ml of water, and the resulting crystal was recovered by filtration, washed with water and dried. Recrystallization with a mixed solvent of chloroform and ethyl acetate produced a crystal of Compound I-61. Yield: 19.7 g, 63.3%. Melting point: 125 - 126 °C.

Result of elementary analysis (C <sub>44</sub> H <sub>66</sub> Cl <sub>4</sub> O <sub>3</sub> S)				
	C	H	Cl	S
Measured data (%)	61.01	7.55	17.00	3.61
Calculated data (%)	61.10	7.69	16.40	3.71

## SYNTHESIS 7 (Synthesis of Compound I-110):

10.3 ml (0.0739 mol) of triethylamine was added to a solution of 15.8 g (0.0672 mol) of ethyl 3,5-dichloro-4-hydroxybenzoate in 158 ml of acetonitrile. Under stirring at 0 °C, 27.3 g (0.0739 mol) of chlorocarbonyl-2-ethyl-2-(2,4-di(1,1-dimethylpropyl)phenoxy)ethyl was added dropwise at room temperature and the mixture was stirred for one hour and a half. To the reaction mixture, 800 ml of ethyl acetate was added and the ethyl acetate layer was washed with a saturated aqueous solution of sodium chloride and dried with Glauber's salt. After the Glauber's salt was filtered off, the filtrate was concentrated under vacuum

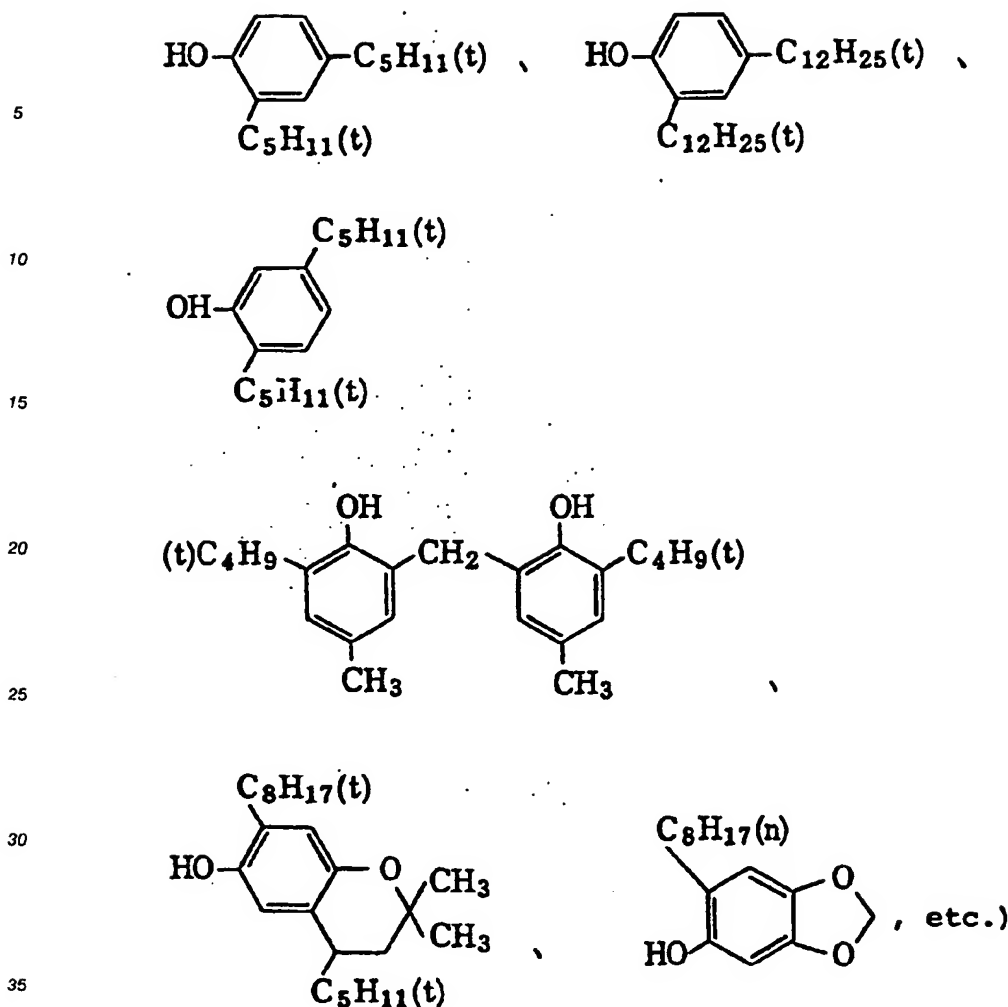
to obtain 42.1 g of Compound I-110 in a crude form. The crude product was purified by column chromatography on silica gel (800 g) using a hexane/ethyl acetate mixture as an eluting solvent under varying concentrations of 100/1 to 20/1. Compound I-110 was obtained as a colorless oil. Yield: 35.8 g, 94%.

Result of elementary analysis (C <sub>30</sub> H <sub>40</sub> Cl <sub>2</sub> O <sub>6</sub> )			
	C	H	Cl
Measured data (%)	63.68	7.06	12.23
Calculated data (%)	63.49	7.10	12.49

Regarding the addition of the compounds used in the present invention, those having a low molecular weight or those which are easily soluble in water can be added to processing solutions so that the compounds can be introduced into photographic materials during the processing procedure. Preferably, the compounds used in the present invention are added to photographic materials during the manufacture procedure. In the latter case, in general, the compound is dissolved in a single high boiling point solvent (oil) (b.p. 170 °C or more under atmospheric pressure) or in a single low boiling point solvent or in a mixed solvent comprising the oil and a low boiling point solvent, and the resulting solution is emulsified and dispersed in an aqueous solution of a hydrophilic colloid such as gelatin to obtain the compound-containing emulsion. The compounds of the present invention are preferably those which are soluble in high boiling point organic solvents. The grain size of the grains in the emulsified dispersion is not specifically limitative but is preferably from 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , especially preferred from 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ . Especially, in view of the effect of the present invention, the compounds used in the present invention are preferably those capable of co-emulsifying with couplers. In this case, the ratio of oil/coupler by weight is preferably from 0.00 to 2.0.

The ratio of the compound used in the present invention in the emulsion is from  $1 \times 10^{-3}$  to 10 mols, preferably from  $3 \times 10^{-2}$  to 5 mols, per mol of coupler.

As specific examples of the above-mentioned oils, there may be mentioned, for example, alkyl phthalates (e.g., dibutyl phthalate, dioctyl phthalate, diisodecyl phthalate, dimethoxyethyl phthalate), phosphates (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctylbutyl phosphate, monophenyl-p-t-butylphenyl phosphate, etc.), citrates (e.g., tributyl acetylcitrate), benzoates (e.g., octyl benzoate), alkylamides (e.g., diethylaurylamide, dibutylaurylamide), fatty acid esters (e.g., dibutoxyethyl succinate, diethyl azelate), trimesates (e.g., tributyl trimesate), epoxy ring-containing compounds (e.g., compounds described in U.S. Patent 4,540,657), phenols (e.g.,



and ethers (e.g., phenoxyethanol, diethylene glycol-monophenylether,).

As low boiling point solvents which are used as an auxiliary solvent, there may be mentioned organic solvents having a boiling point of from 30°C to 150°C under atmospheric pressure, for example, lower alkyl acetates such as ethyl acetate, isopropyl acetate and butyl acetate as well as ethyl propionate, methanol, ethanol, secondary butyl alcohol, cyclohexanol, fluorinated alcohols, methylisobutylketone,  $\beta$ -ethoxyethyl acetate, methylcellosolve acetate, acetone, methyl acetone, acetonitrile dioxane, dimethylformamide, dimethylsulfoxide, chloroform, cyclohexane..

45 In place of the high boiling point organic solvents, not only oily solvents of additives such as couplers (including substances which are solid at room temperature, such as wax,) but also latex polymers can be used. Otherwise, additives themselves, such as couplers, color mixing preventing agents, ultraviolet absorbers,, can be used as oily solvents.

As the latex polymers, those obtained from one or more monomers selected from acrylic acid, 50 methacrylic acid and esters thereof (e.g., methyl acrylate, ethyl acrylate, butyl methacrylate.), acrylamide, methacrylamide, vinyl esters (e.g., vinyl acetate, vinyl propionate.), acrylonitrile, styrene, divinylbenzene, vinyl-alkylethers (e.g., vinyl-ethylether.), maleates (e.g., methyl maleate), N-vinyl-2-pyrrolidone, N-vinylpyridine, 2- and 4-vinylpyridine,. The monomers can be used singly or in mixtures thereof.

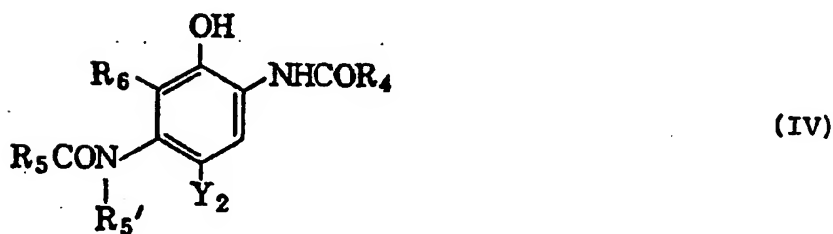
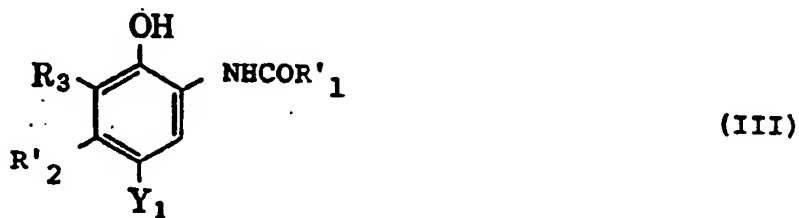
As examples of surfactants to be used for dispersing the solution containing the compound used in the present invention singly or in the form of a mixture with a coupler into an aqueous protective colloid 55 solution, there may be mentioned saponin as well as sodium alkyl-sulfosuccinates, sodium alkylbenzene-sulfonates..

The compounds used in the present invention can be used in the form of a mixture with a yellow

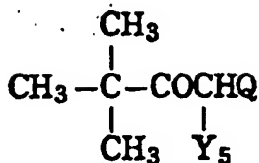
coupler, a magenta coupler or a cyan coupler. In particular, the combined use of the compounds together with a magenta coupler is preferred for sufficiently attaining the effect of the present invention.

The couplers to be used in combination with the compound used in the present invention may be either 4-equivalent or 2-equivalent to silver ion and may also be in the form of a polymer or an oligomer. In addition, the couplers for use in combination may be either single or in the form of a mixture of two or more of the couplers.

Preferred examples of the couplers for use in the present invention are those represented by the following formulae:







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In these formulae, R<sub>1</sub>, R<sub>4</sub> and R<sub>5</sub> each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R<sub>2</sub> represents an aliphatic group; R<sub>3</sub> and R<sub>6</sub> each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic-oxy group or an acylamino group; R<sub>5</sub>' represents a hydrogen atom or has the same meaning as R<sub>5</sub>; R<sub>7</sub> and R<sub>9</sub> each represents a substituted or unsubstituted phenyl group; R<sub>8</sub> represents a hydrogen atom, an aliphatic or aromatic acyl group or an aliphatic or aromatic sulfonyl group; R<sub>10</sub> represents a hydrogen atom or a substituent; Q represents a substituted or unsubstituted N-phenylcarbamoyl group; Z<sub>a</sub> and Z<sub>b</sub> each represents a methine group, a substituted methine group or =N-; Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub>, Y<sub>4</sub> and Y<sub>5</sub> each represents a hydrogen atom or a group capable of being removed in a coupling reaction with an oxidized product of a developing agent (hereinafter referred to as a "removing group").

In the formula (III), the typical examples of the substituents and those coupler are those described in U.S. Patents 4,518,687, 4,511,647, 3,772,002 and 4,564,590, Canadian Patent 625,822, and Japanese Patent Application (OPI) Nos. 39045/86 and 70846/87.

In the formula (IV), the typical examples of the substituents and these couplers are as described in U.S. Patents 2,772,162, 2,895,826, 4,334,011, 4,500,635, 4,565,777, 4,124,396 and 4,613,564, and Japanese Patent Application (OPI) No. 164555/84.

In the formulae (III) and (IV), R<sub>2</sub> and R<sub>3</sub>, and R<sub>5</sub> and R<sub>6</sub> each may form a 5-, 6- or 7-membered ring as described in U.S. Patents 4,327,173, 4,564,586 and 4,430,423, and Japanese Patent Application (OPI) No. 390441/86. Further, the typical examples of cyan couplers having an ureido group are those described in U.S. Patents 4,333,999, 4,451,559, 4,444,872, 4,427,767 and 4,579,813, and European Patent 067,689 B1.

In the formula (V), the typical examples of the substituents and these couplers are those described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, 3,936,015, 4,310,619 and 4,351,897.

In the formula (VI), the typical examples of the substituents and these couplers are those described in U.S. Patents 4,500,630 and 4,540,654, Japanese Patent Application (OPI) Nos. 65245/86, 65246/86 and 147254/86, and European Patent 226,849.

In the formula (VIII), the typical examples of the substituents and these couplers are those described in U.S. Patents 4,622,287, 4,623,616, 3,408,194, 3,933,501, 4,046,575, 4,133,958 and 4,401,752.

In addition, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, or Y<sub>1</sub>; R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> or Y<sub>2</sub>; R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> or Y<sub>3</sub>; R<sub>10</sub>, Z<sub>a</sub>, Ab or Y<sub>4</sub>; and Q or Y<sub>5</sub> may form a dimer or higher polymer.

The aliphatic group as referred to herein means a linear, branched or cyclic alkyl, alkenyl or alkynyl group.

Specific examples of the couplers of the formulae (III) and (IV) are set forth below.

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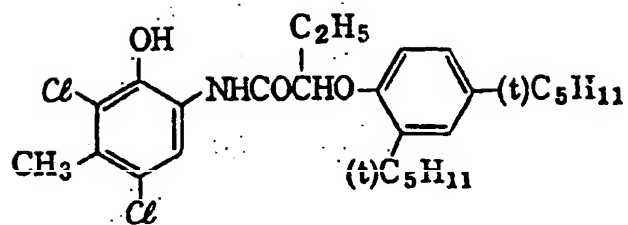
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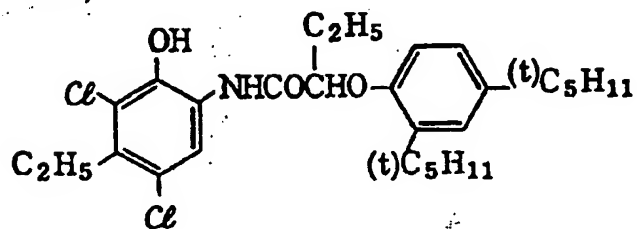
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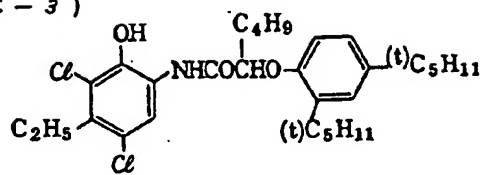
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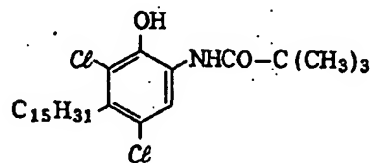
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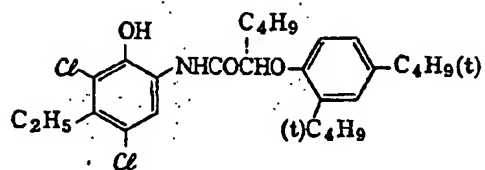
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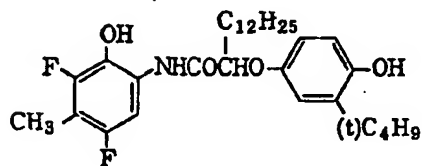
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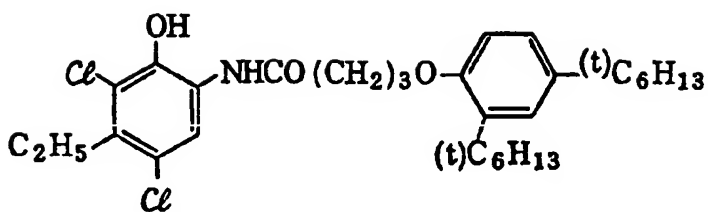
( C - 5 )



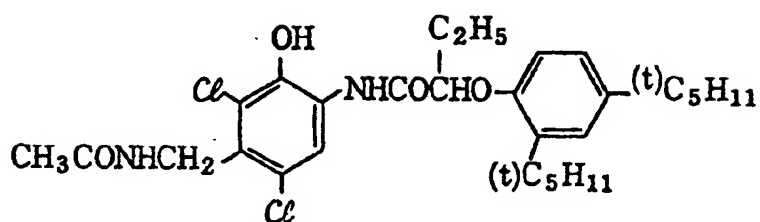
( C - 6 )



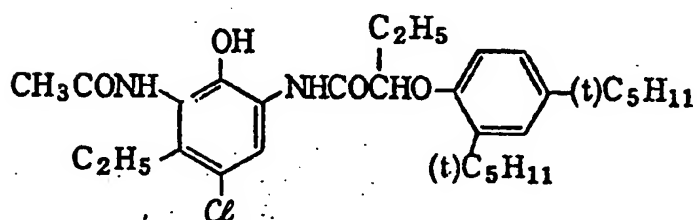
( C - 7 )



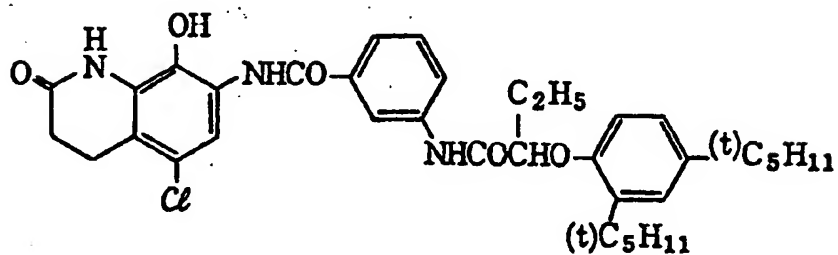
( C - 8 )



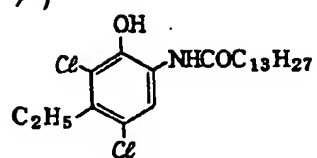
( C - 9 )



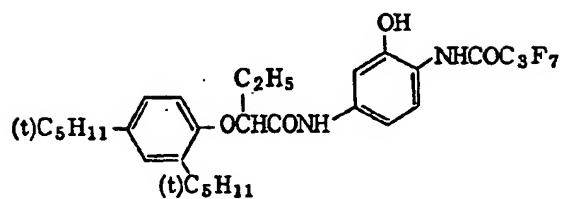
( C - 10 )



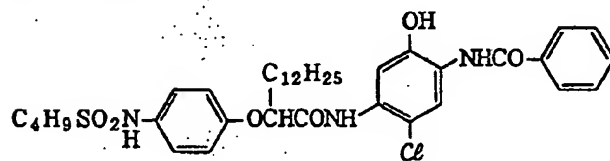
( C - / / )



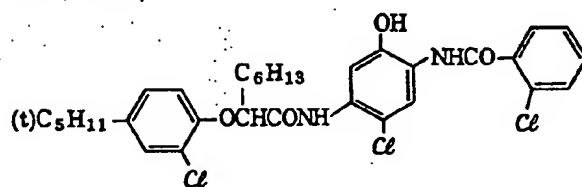
( C - / 2 )



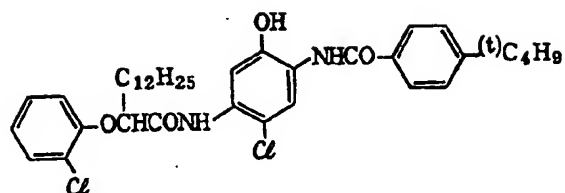
( C - / 3 )



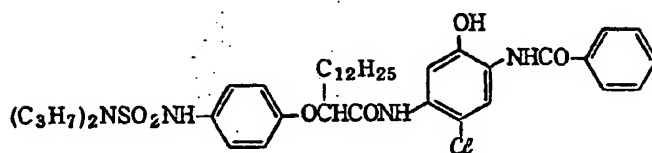
( C - / 4 )



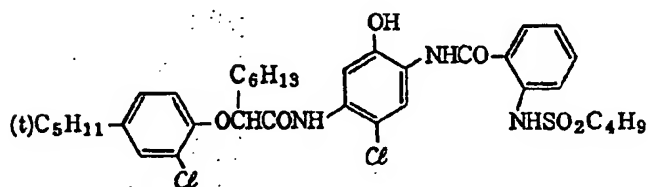
( C - 15 )



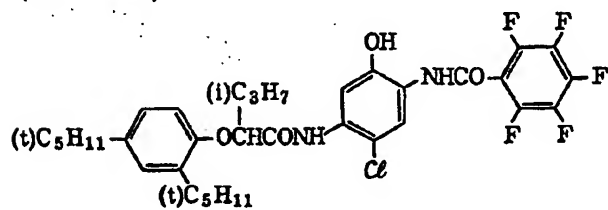
( C - 16 )



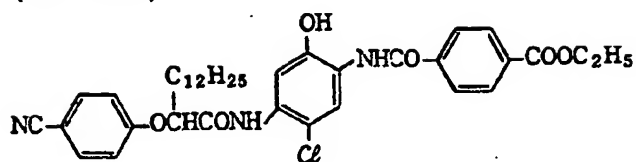
( C - 17 )



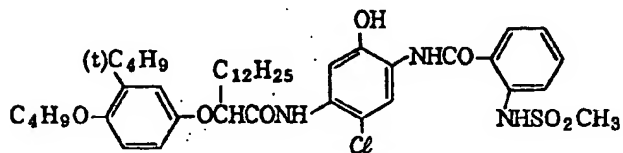
( C - 18 )



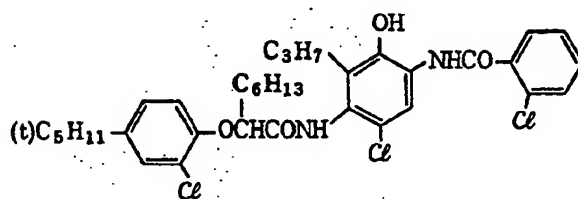
( C - 1 9 )



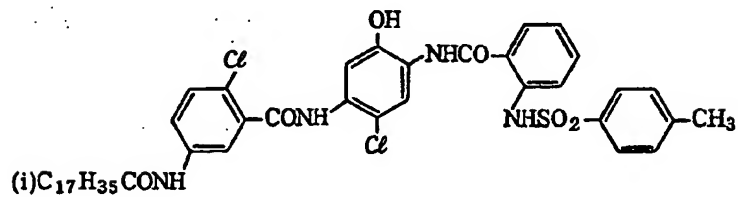
( C - 2 0 )



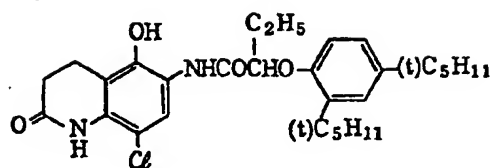
( C - 2 1 )



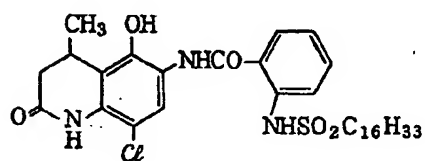
( C - 2 2 )



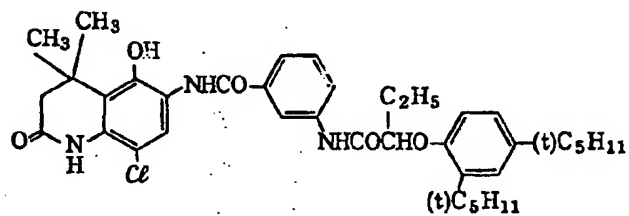
( C - 2 3 )



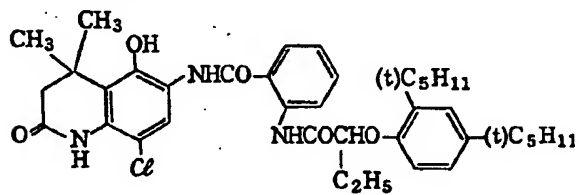
( C - 2 4 )



( C - 2 5 )

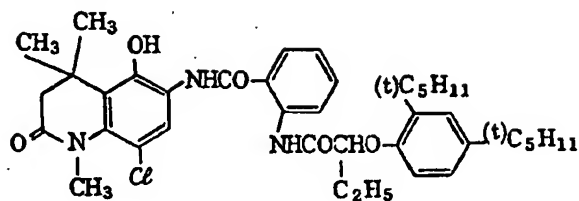


( C - 2 6 a )

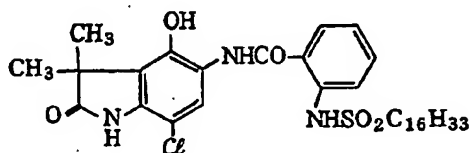




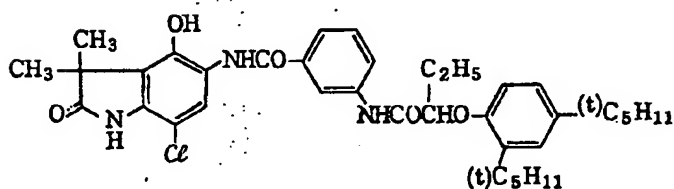
( C - 2 6 b )



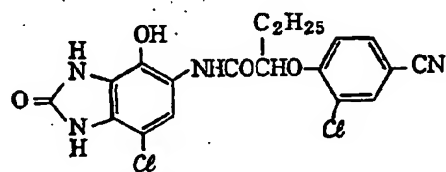
( C - 2 7 )



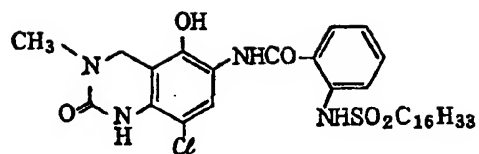
( C - 2 8 )



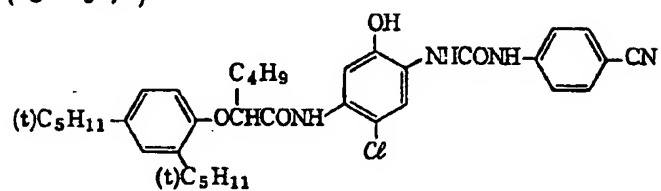
( C - 2 9 )



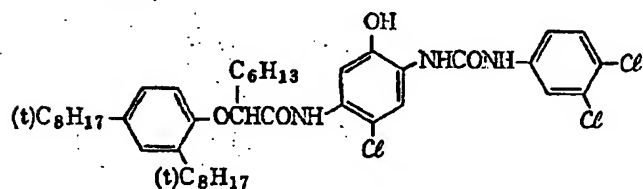
( C - 3 0 )



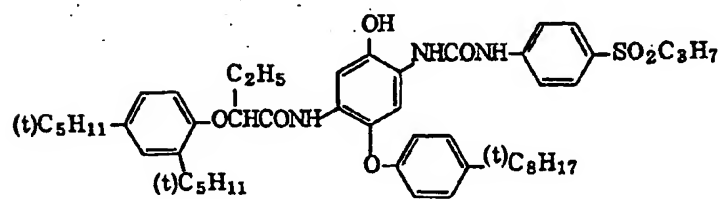
( C - 3 1 )



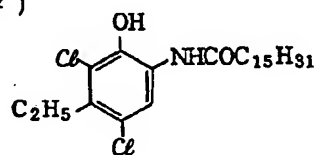
( C - 3 2 )



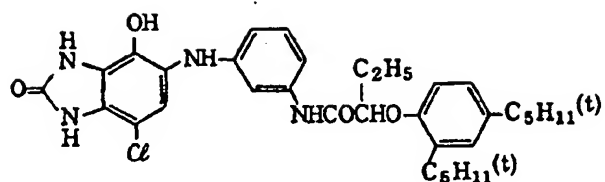
( C - 3 3 )



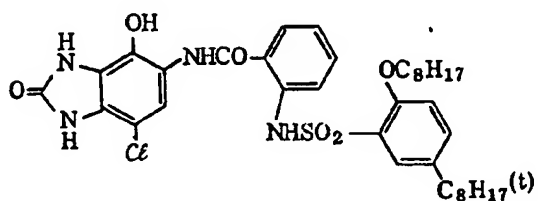
( C - 3 4 )



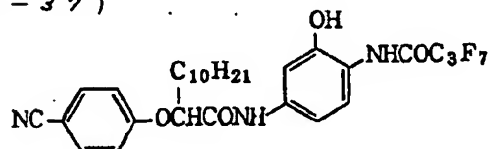
( C - 3 5 )



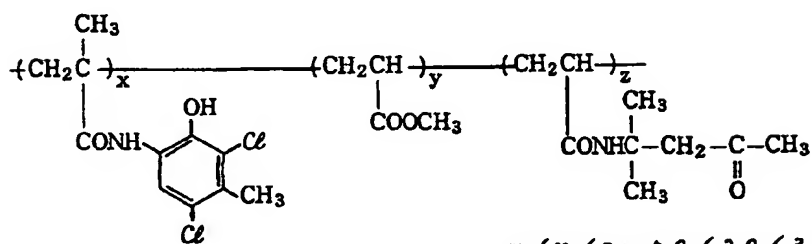
( C - 3 6 )



( C - 3 7 )



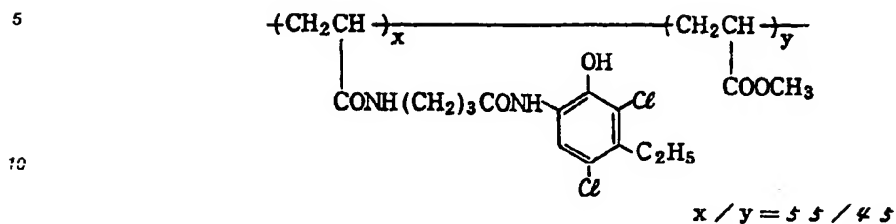
( C - 3 8 )



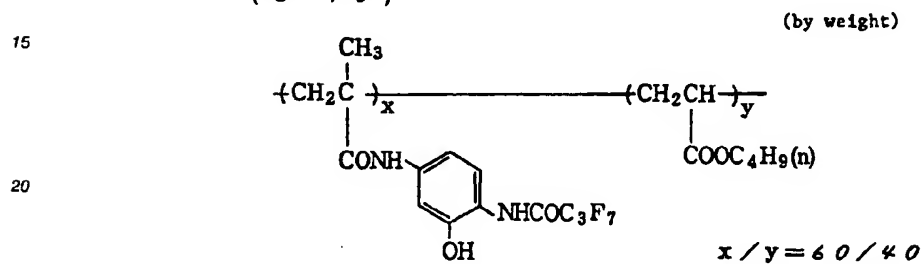
$$x / y / z = 50 / 20 / 30$$

(by weight)

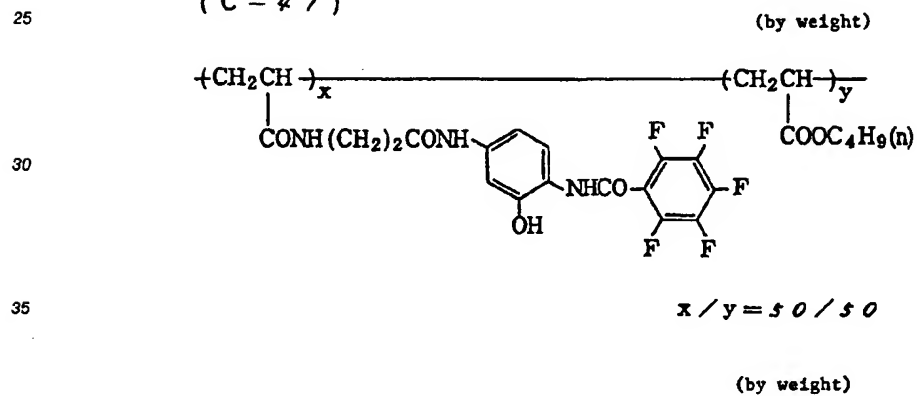
( C - 3 9 )



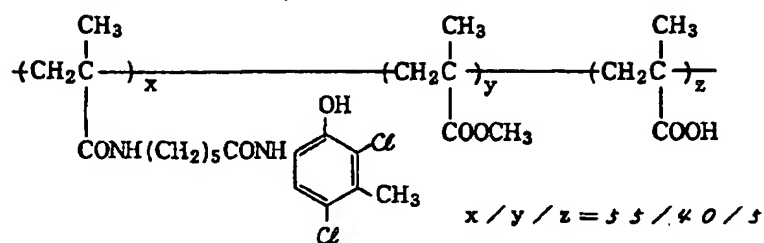
( C - 4 0 )



( C - 4 1 )

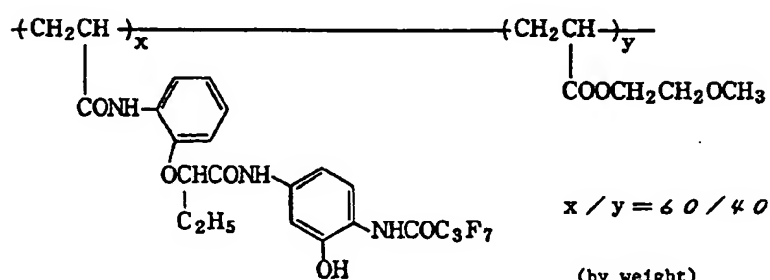


( C - 4 2 )



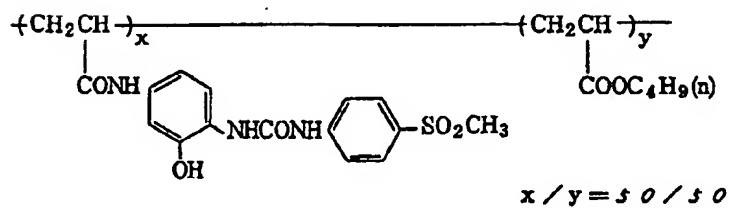
( C - 4 3 )

(by weight)



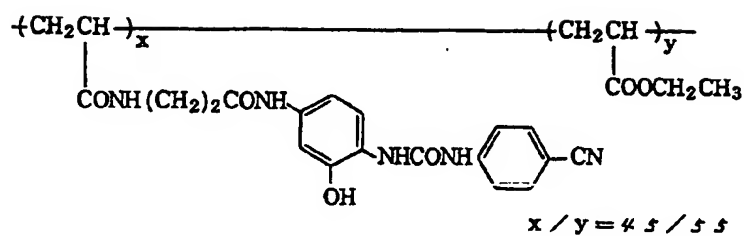
(by weight)

( C - 4 4 )



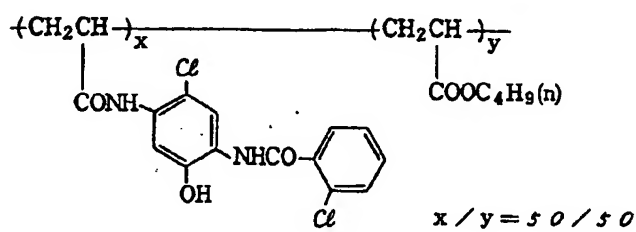
(by weight)

( C - 4 5 )



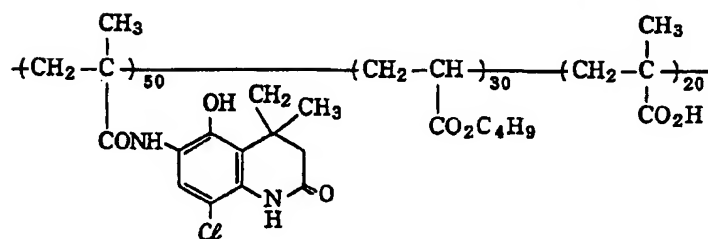
( C - 4 6 )

(by weight)

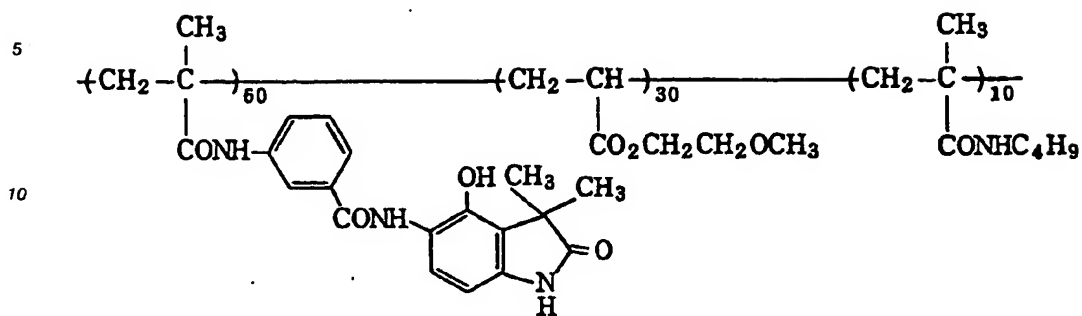


( C - 4 7 )

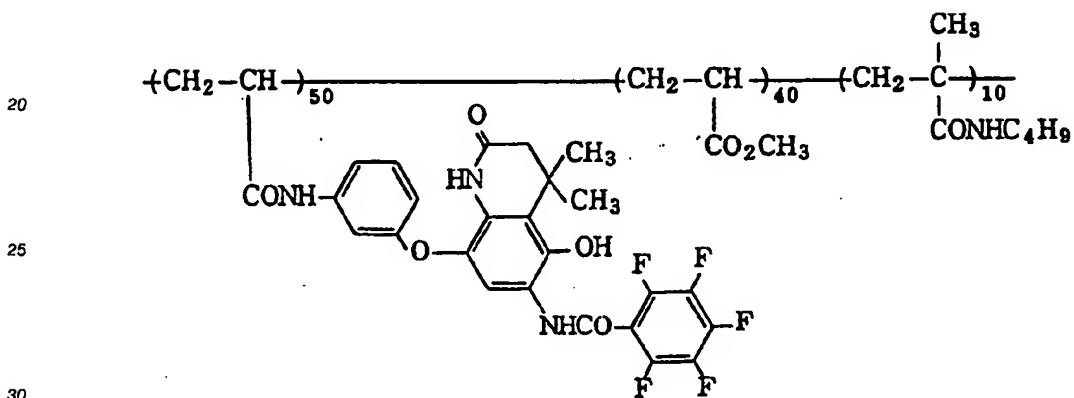
(by weight)



( C - 48 )

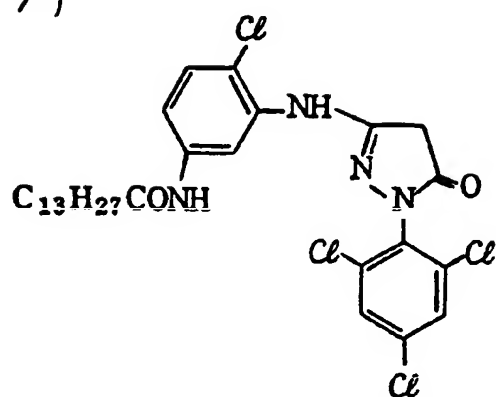


( C - 49 )

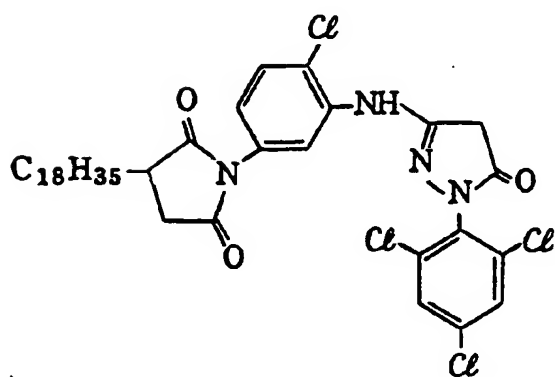


Specific examples of the couplers of the formulae (V) and (VI) are set forth below.

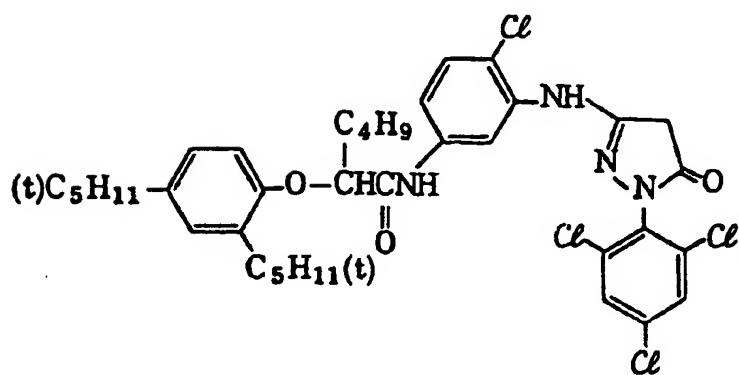
( M - 1 )



( M - 2 )

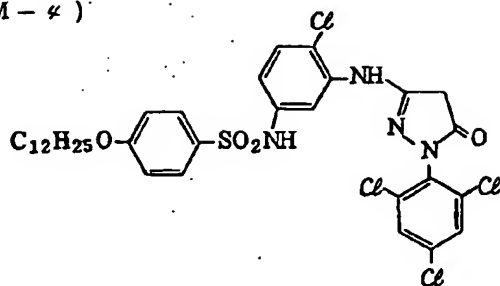


( M - 3 )

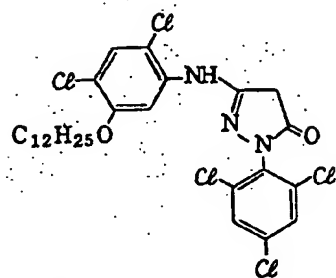




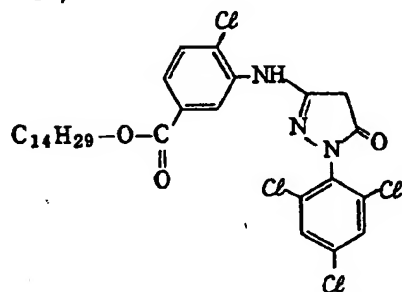
( M - 4 )



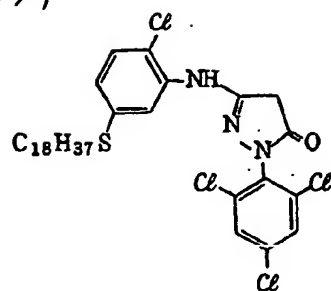
( M - 5 )



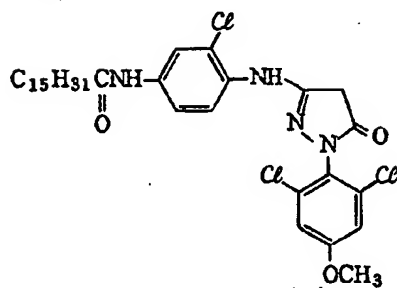
( M - 6 )



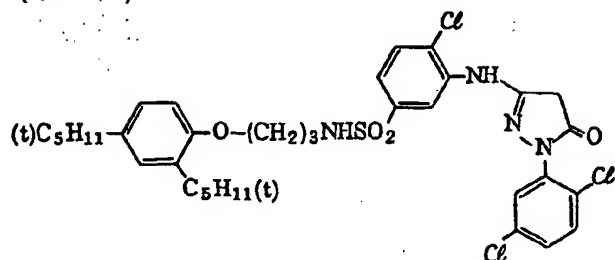
( M - 7 )



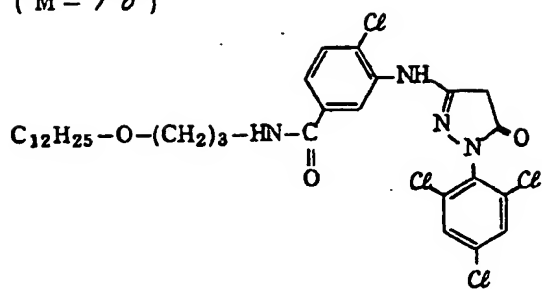
( M - 8 )



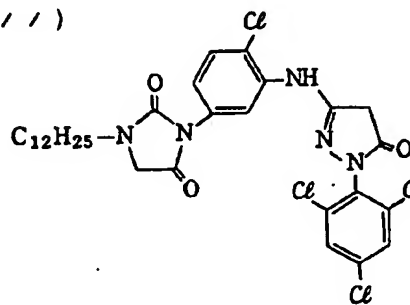
( M - 9 )



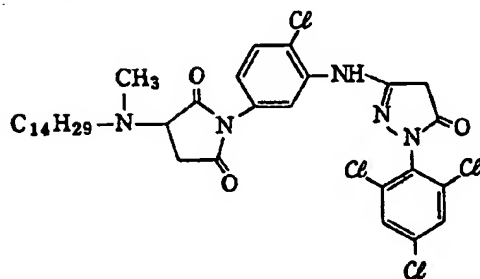
( M - / 0 )



( M - / / )

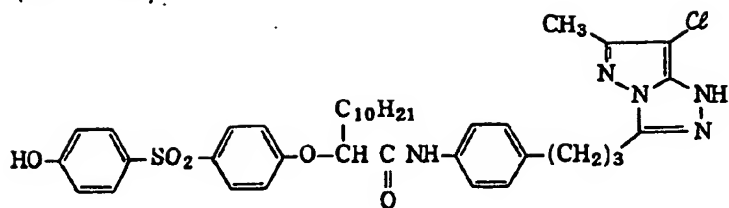


( M - / 2 )

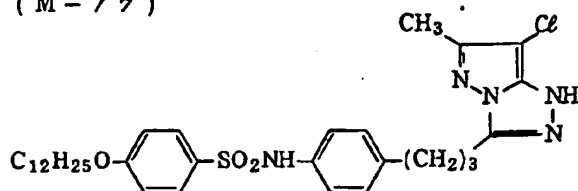


CCCCCCCCCCCCCCCC(=O)Nc1ccc(NC2=C(Sc3ccc(OC)cc3)N(=O)C2=O)c(Cl)c1CCCCCc1ccc(OCC(C)CNC(=O)Nc2ccc(Cl)cc2)c(Cl)c1CCCCC >> CCCCC1=CC=C(C=C1)OCC(C)CNC(=O)Nc2ccc(Cl)cc2C3=C(Cl)C(Cl)=CC(Cl)=C3C4=C(Cl)C(Cl)=CC(Cl)=C4SC5=CC=C(C=C5)OCCOCCOCCCCCCCc1ccc(Cl)cc1OC(CCCC)C(=O)Nc2ccc(Cl)cc2Nc3nc4c(ncn3C4=O)c5cc(Cl)c(Cl)c(Cl)c5

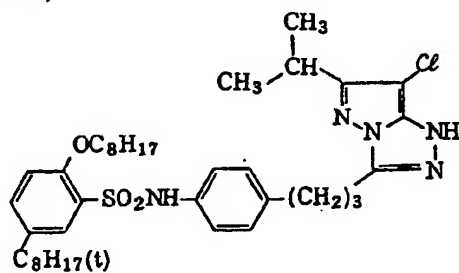
( M - / 6 )



( M - / 7 )



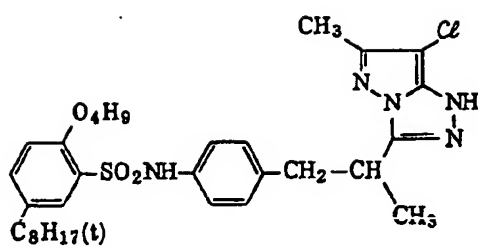
( M - / 8 )



( M - 1 9 )

5

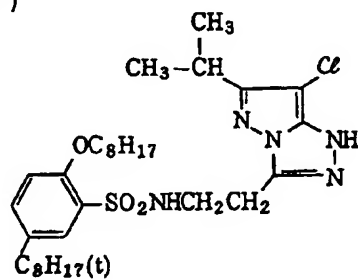
10



( M - 2 0 )

15

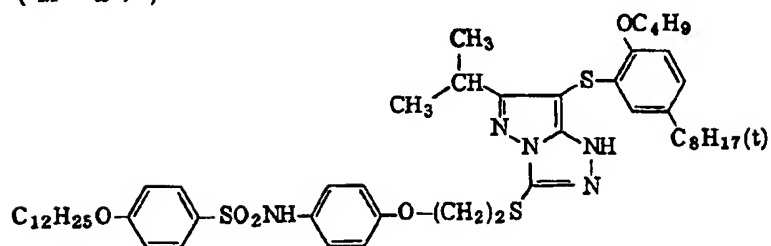
20



( M - 2 1 )

25

30



35

40

45

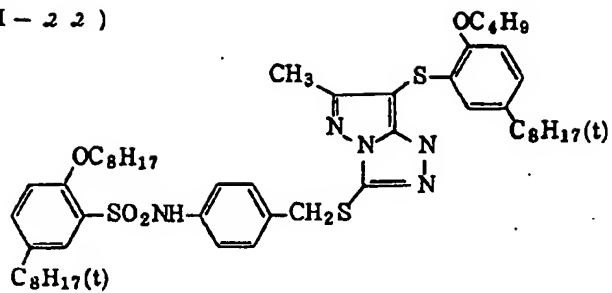
50

55

( M - 2 2 )

5

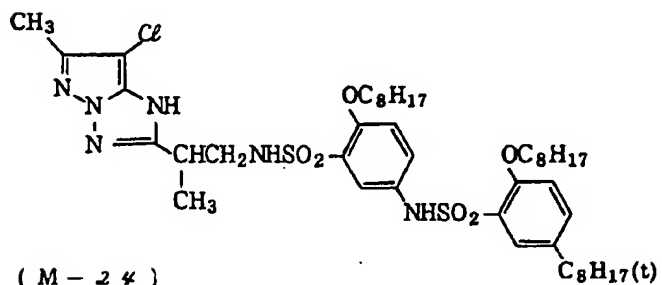
10



( M - 2 3 )

15

20



( M - 2 4 )

25

30

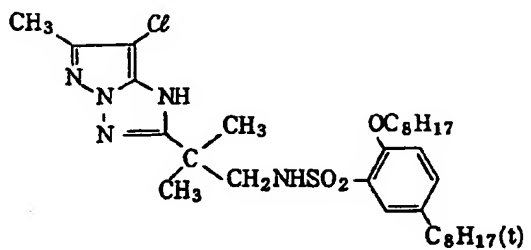
35

40

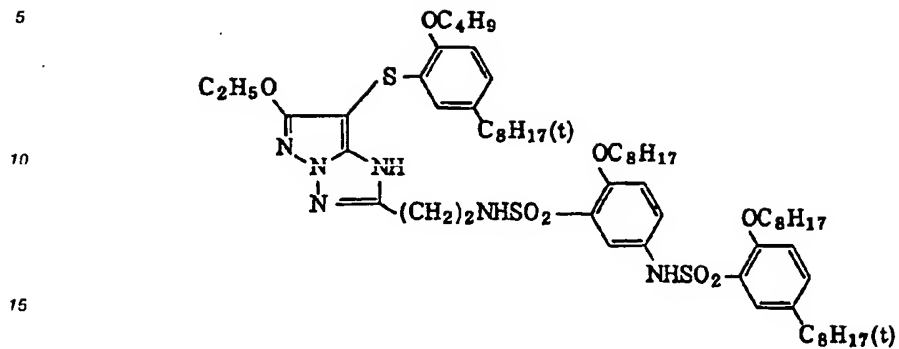
45

50

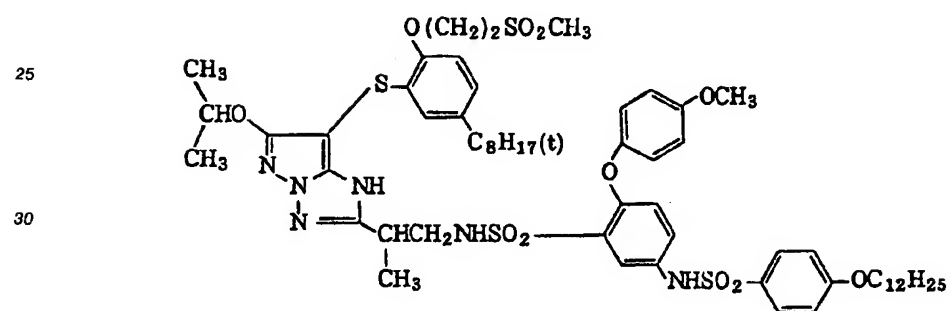
55



( M - 2 5 )

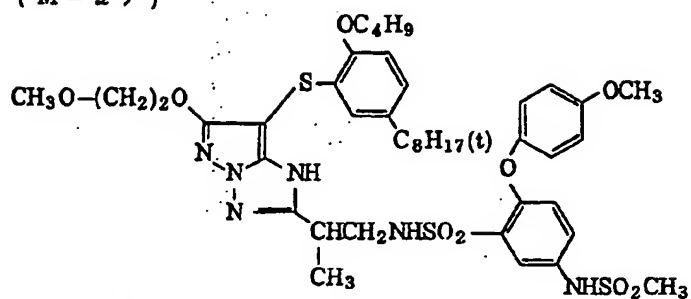


( M - 2 6 )

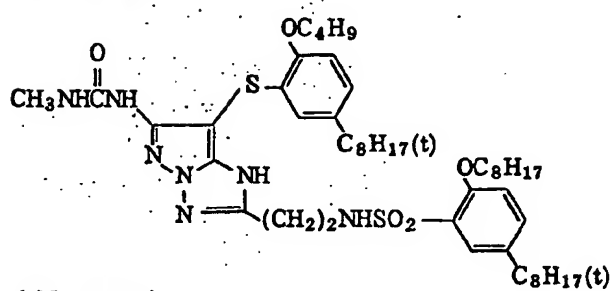




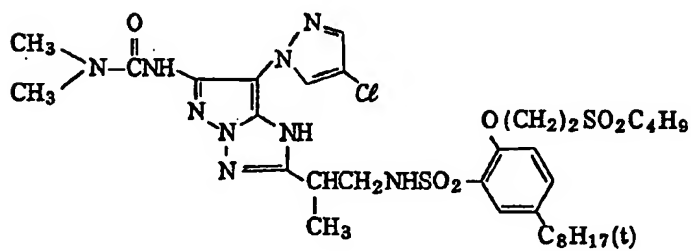
( M - 2 7 )



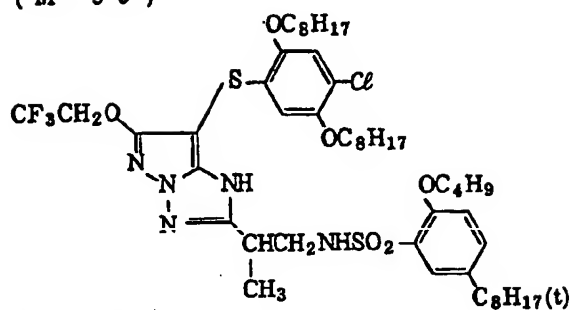
( M - 2 8 )



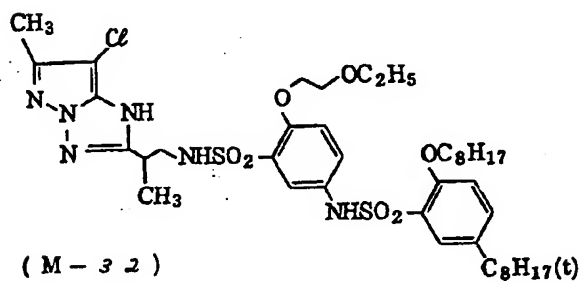
( M - 2 9 )



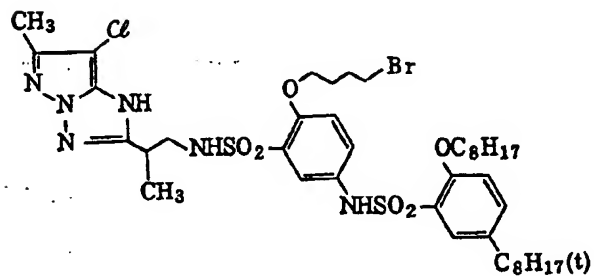
( M - 3 0 )



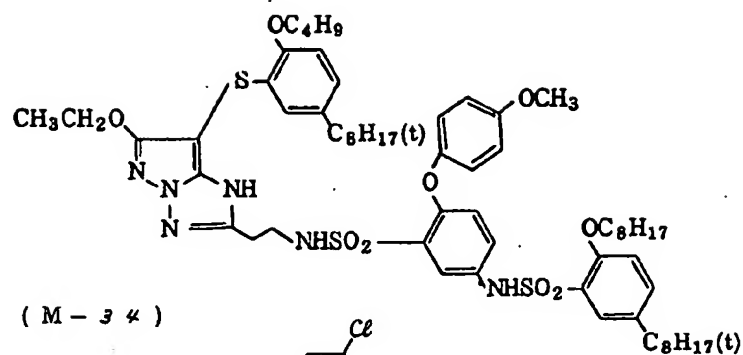
( M - 3 1 )



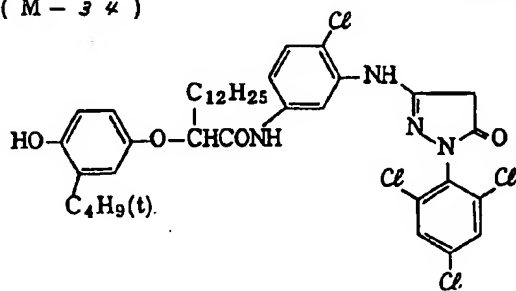
( M - 3 2 )



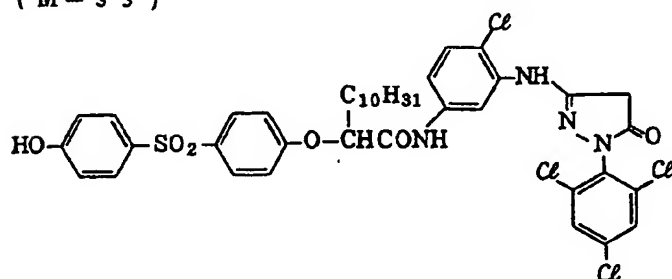
( M - 3 3 )



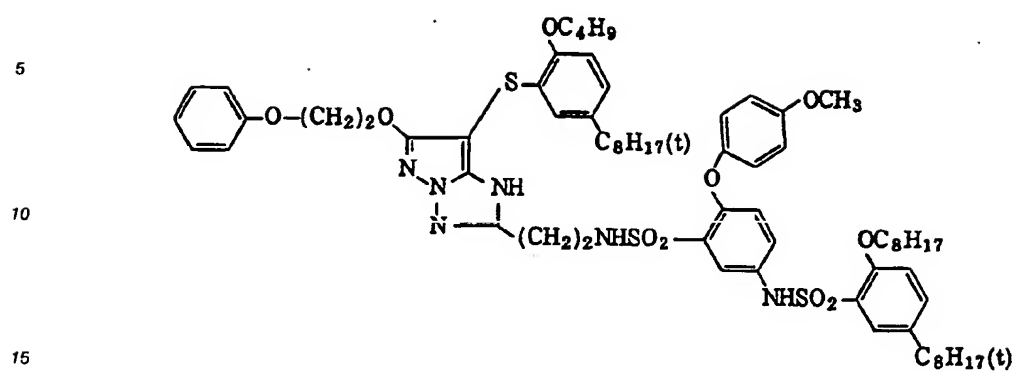
( M - 3 4 )



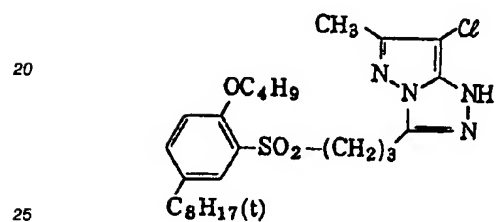
( M - 3 5 )



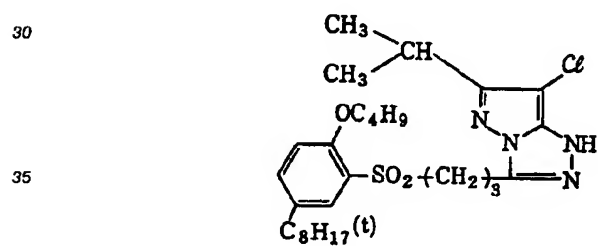
( M - 3 6 )



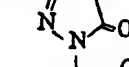
( M - 3 7 )



( M - 3 8 )



$$\begin{array}{c} \text{CH}_3 \\ | \\ +\text{CH}_2\text{C}-\text{ }_x \\ | \\ \text{CONH} \end{array} \text{---} \begin{array}{c} \text{CH}_2\text{CH}-\text{ }_y \\ | \\ \text{COOCH}_3 \end{array} \text{---} \begin{array}{c} \text{CH}_2\text{CH}-\text{ }_z \\ | \\ \text{COOC}_4\text{H}_9\text{(n)} \end{array}$$



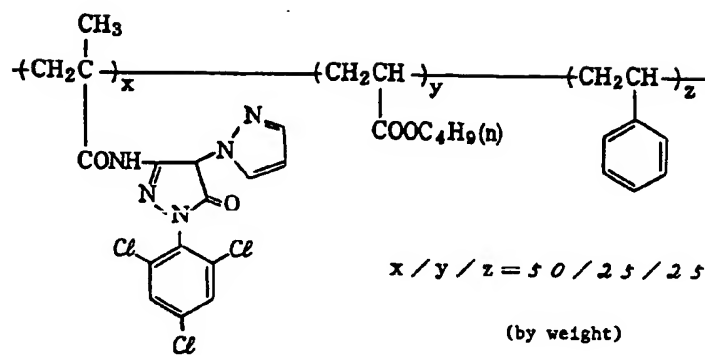
$x / y / z = 50 / 25 / 25$

(by weight)

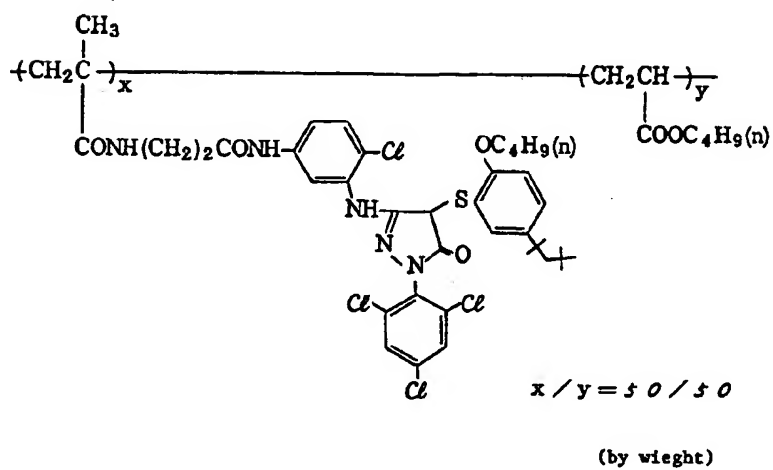
$$\begin{array}{c} \text{-(CH}_2\text{CH)}_x\text{-} \\ | \\ \text{CONH-} \langle \text{C}_6\text{H}_3\text{Cl}_2 \text{NH} \rangle \text{-} \\ | \\ \text{NH} \langle \text{C}_4\text{H}_3\text{N}_2\text{O} \rangle \text{C=O} \\ | \\ \text{Cl} \langle \text{C}_6\text{H}_2\text{Cl}_3 \rangle \text{Cl} \\ | \\ \text{Cl} \end{array} \quad \text{-(CH}_2\text{CH)}_y\text{-} \\ | \\ \text{COOC}_4\text{H}_9\text{(n)}$$

$x/y = 50/50$   
(by weight)

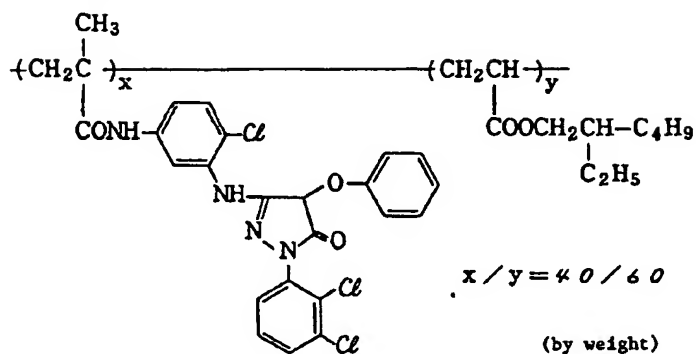
( M - 4 / )



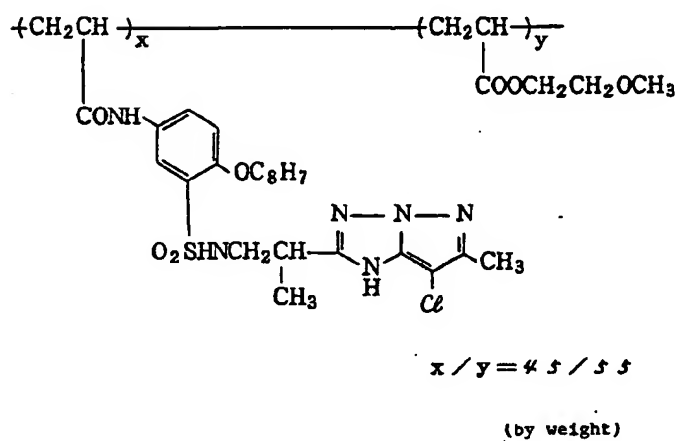
( M - 4 2 )



( M - 43 )



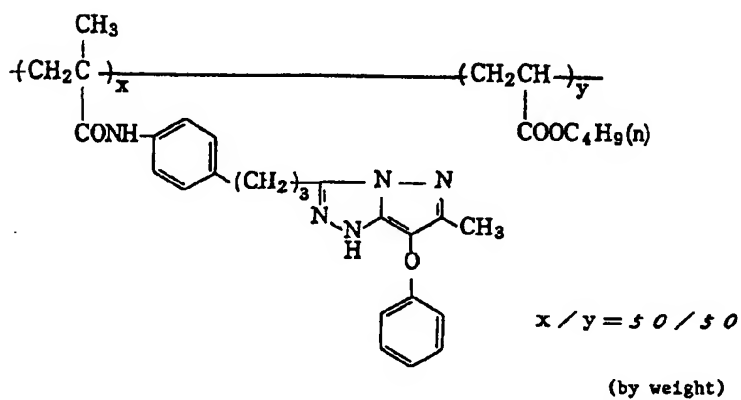
( M - 44 )



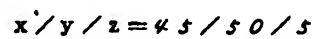
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{-(CH}_2\text{C-)}_x \\ | \\ \text{CONH-} \langle \text{benzene ring} \rangle \text{-(CH}_2\text{)}_2 \text{-N=N-N} \\ | \qquad \qquad \qquad | \qquad \qquad \qquad | \\ \text{H} \qquad \qquad \qquad \text{Cl} \qquad \qquad \qquad \text{CH}_3 \\ | \\ \text{COOC}_4\text{H}_9 \end{array} \text{-(CH}_2\text{CH-)}_y \text{-(CH}_2\text{C-)}_z \begin{array}{c} \text{CH}_3 \\ | \\ \text{COOH} \end{array}$$

$x/y/z = 50/45/5$

( M - 4 6 )

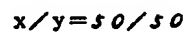




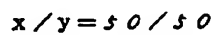


(by weight)

( M - 48 )

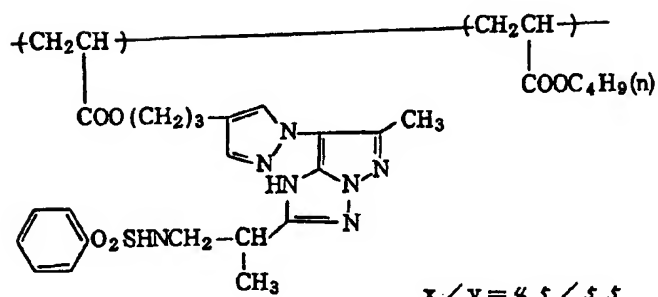


(by weight)



(by weight)

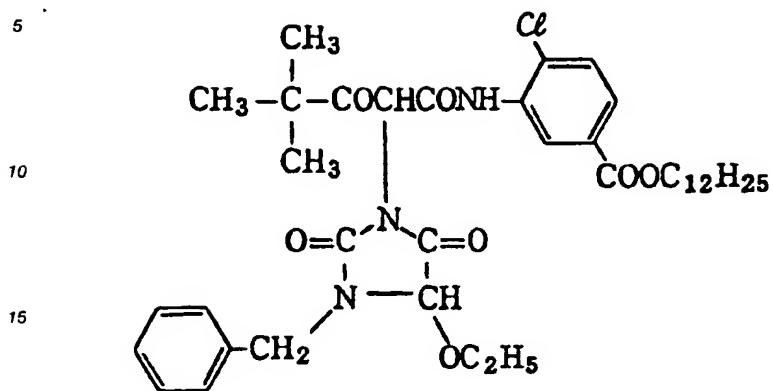
( M - 50 )



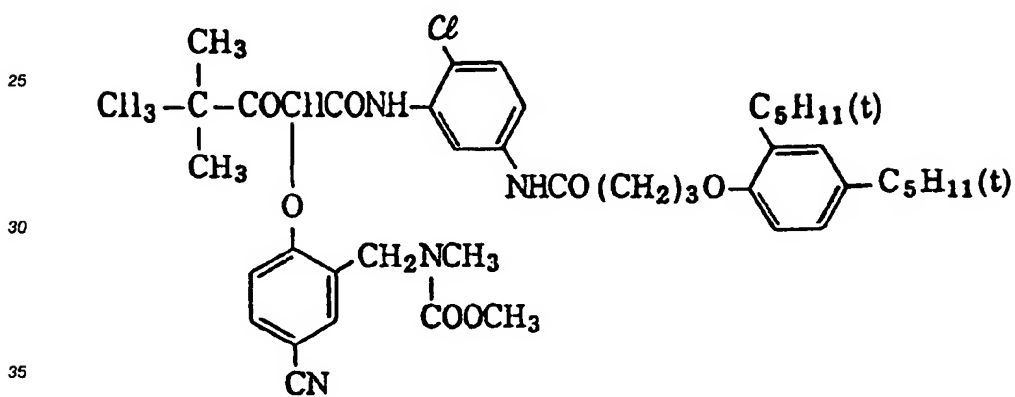
(by weight)

78

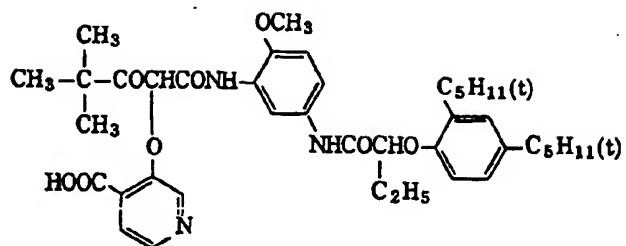
( Y - 1 )



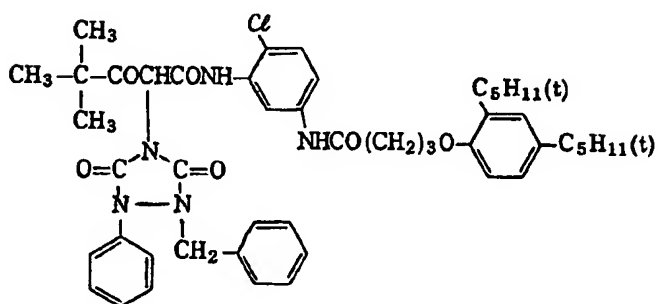
( Y - 2 )



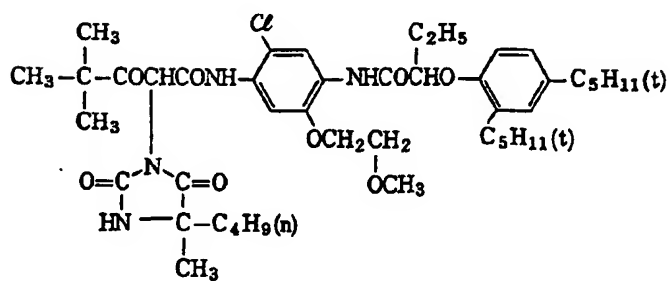
( Y - 3 )



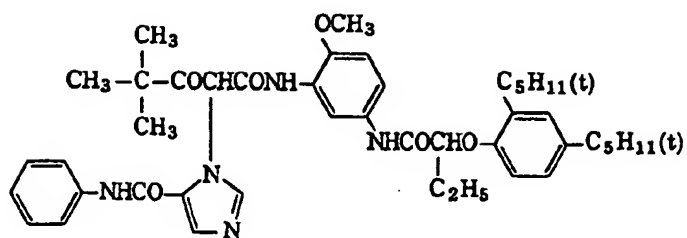
( Y - 4 )



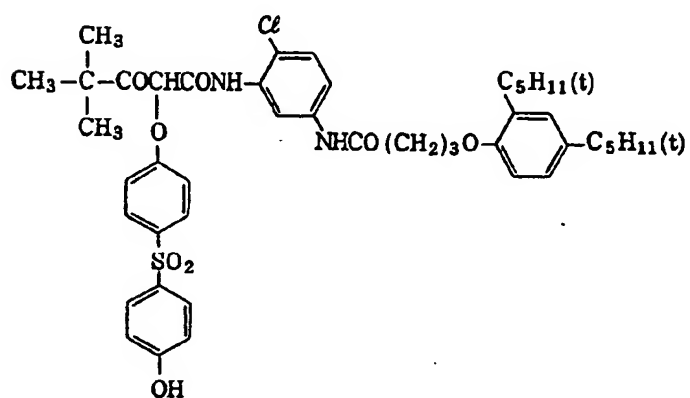
( Y - 5 )



( Y - 6 )

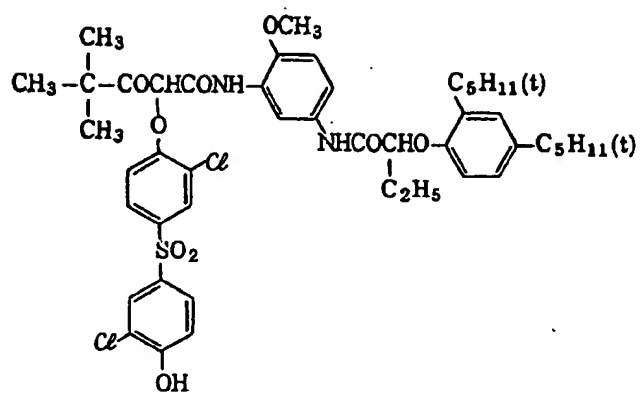


( Y - 7 )

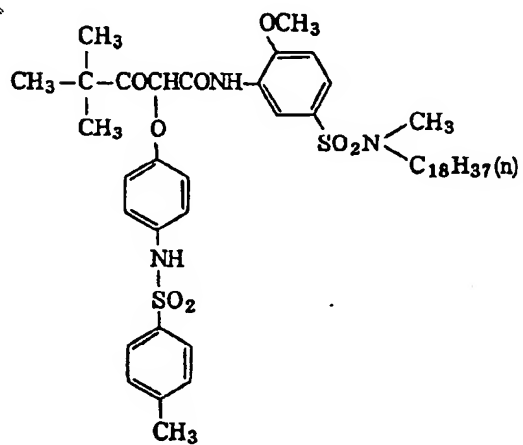


CC(C)C(=O)CNC1=CC=C(C=C1)C(=C(C=C1)OC)C(Cl)=C1C(=O)NCC(=O)OCC1=CC=C(C=C1)NS(=O)(=O)CCCC1=CC=C(C=C1)OS(=O)(=O)C2=CC=C(C=C2)OC3=CC=C(C=C3)COCC4=CC=CC=C4CC(C)(C)C(=O)Nc1ccc(Cl)cc1NC(=O)OCCCOc2ccc(CCCCCC)cc2

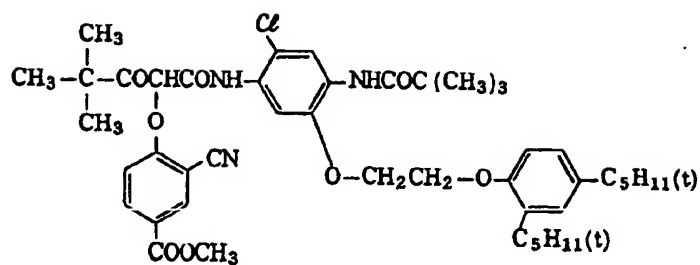
( Y - / o )



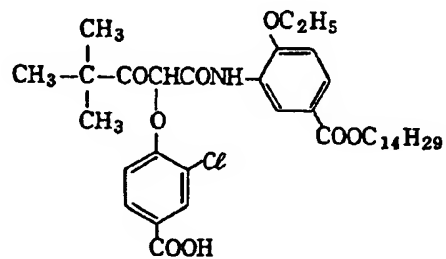
( Y - / / )



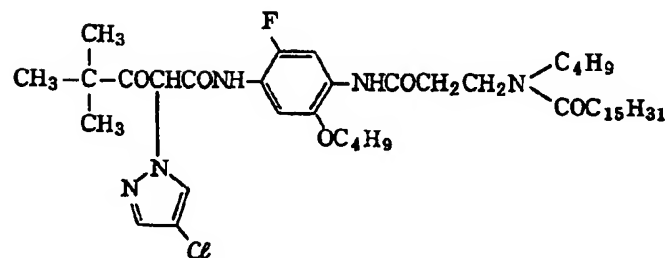
( Y - / 2 )



( Y - / 3 )

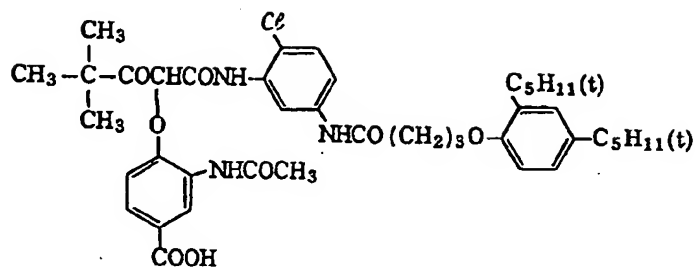


( Y - / 4 )

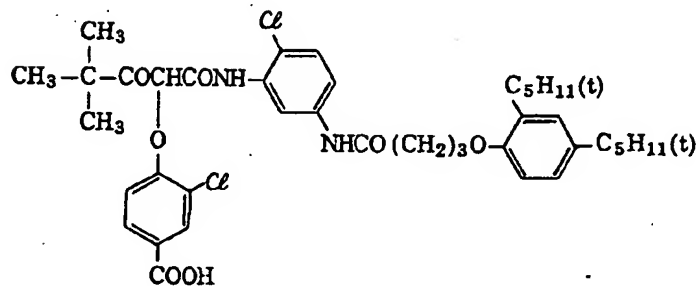




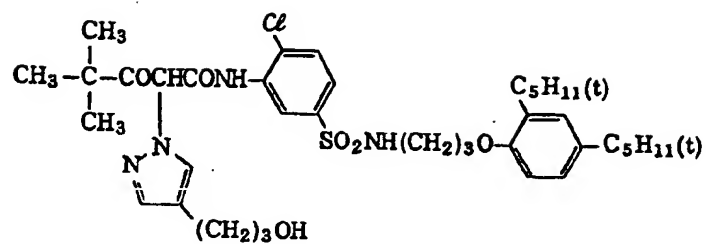
( Y - / 5 )



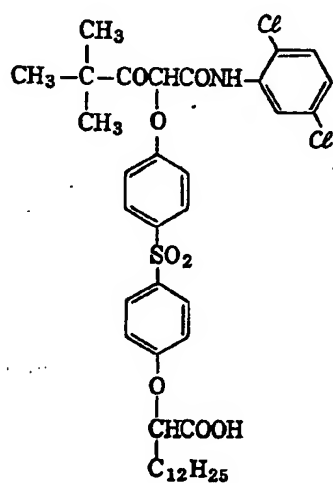
( Y - / 6 )



( Y - 17 )



( Y - 18 )





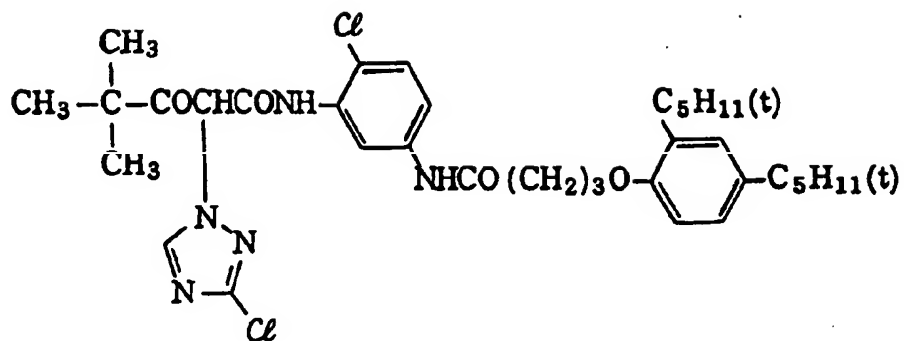
( Y - 2 / )

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( Y - 2 2 )

30

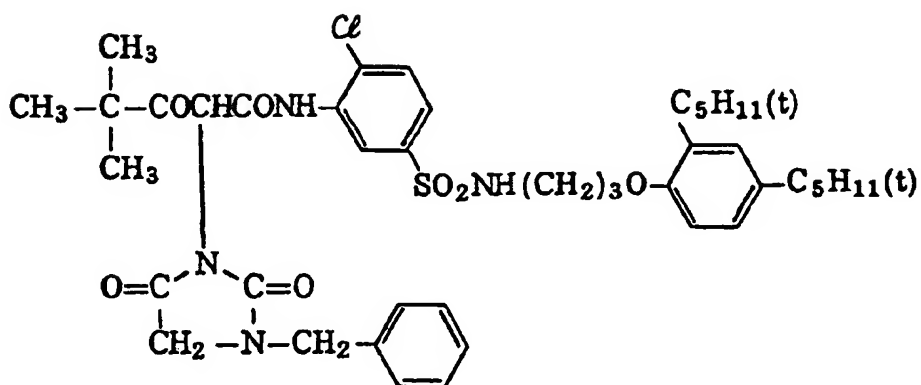
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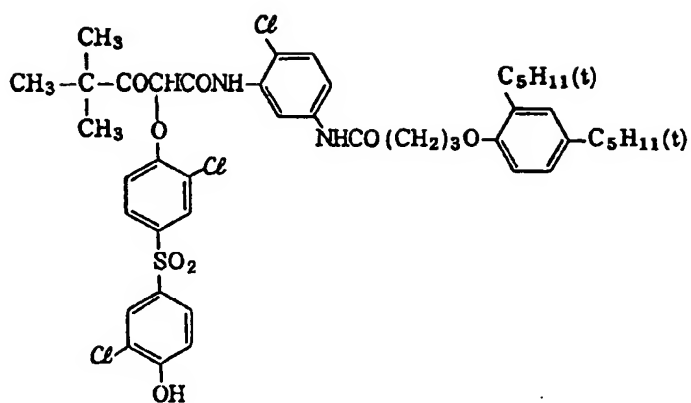
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50

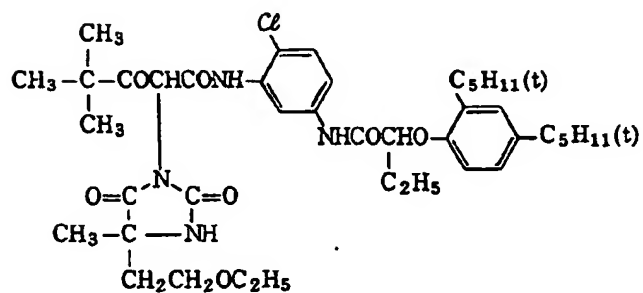
55



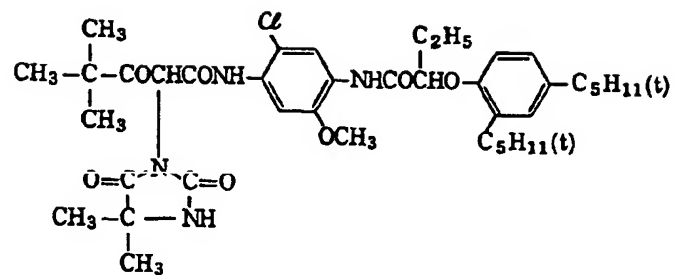
( Y - 2 3 )



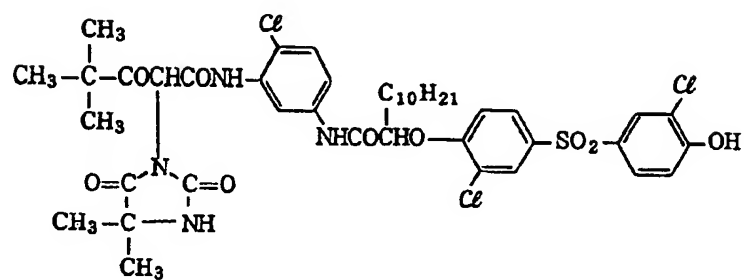
( Y - 2 4 )



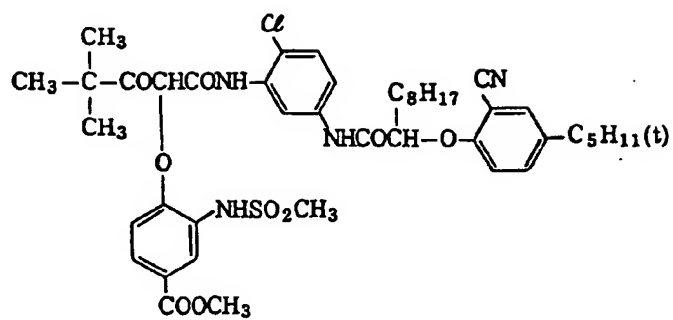
( Y - 2 5 )



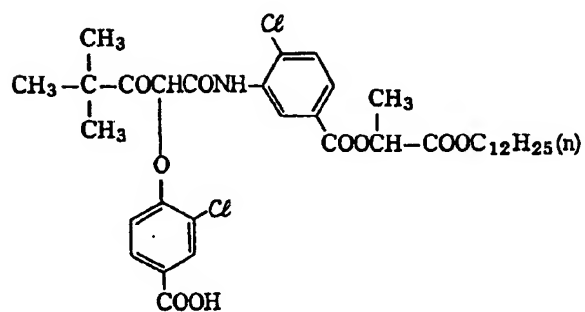
( Y - 2 6 )



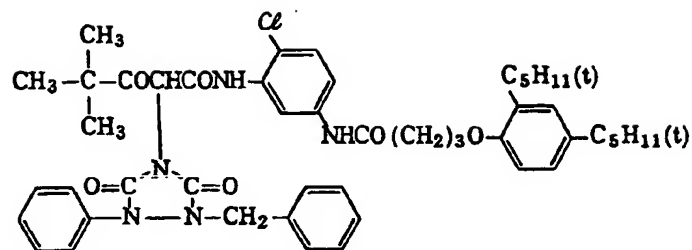
( Y - 2 7 )



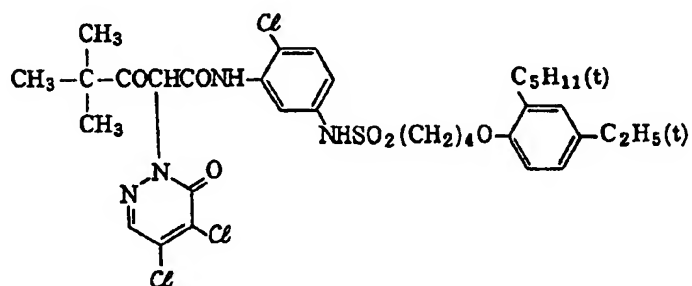
( Y - 2 8 )



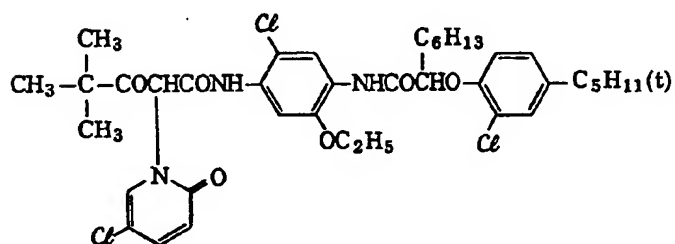
( Y - 2 9 )



( Y - 3 0 )

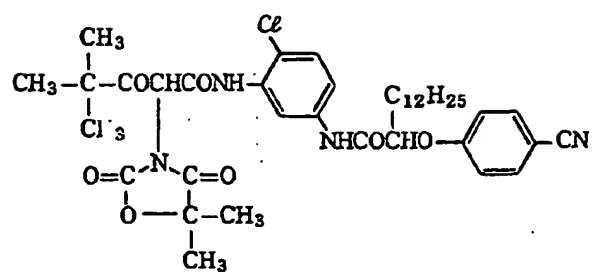


( Y - 3 1 )

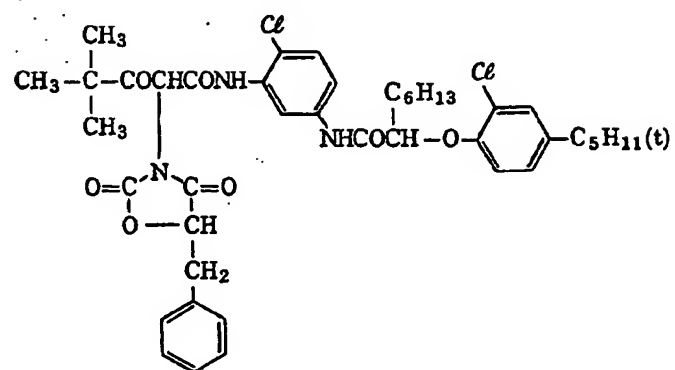




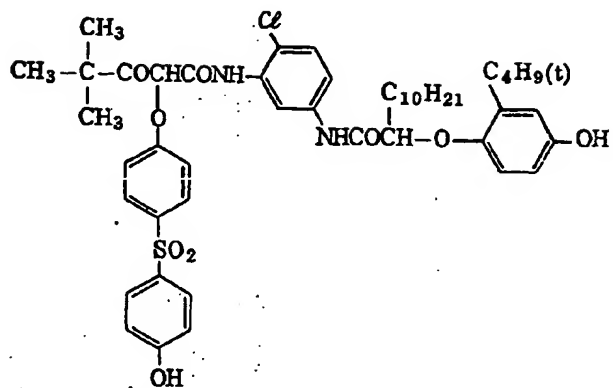
( Y - 3 2 )



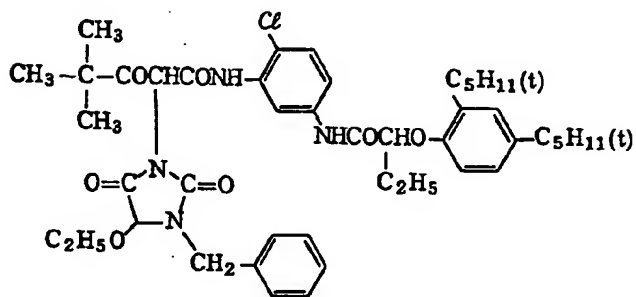
( Y - 3 3 )



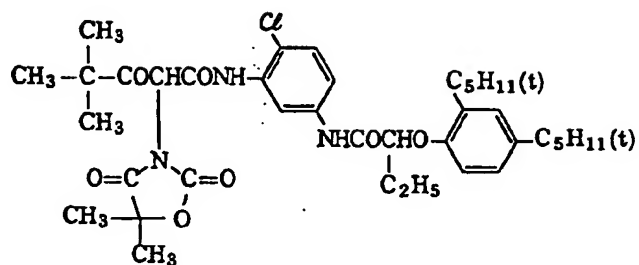
( Y - 3 4 )



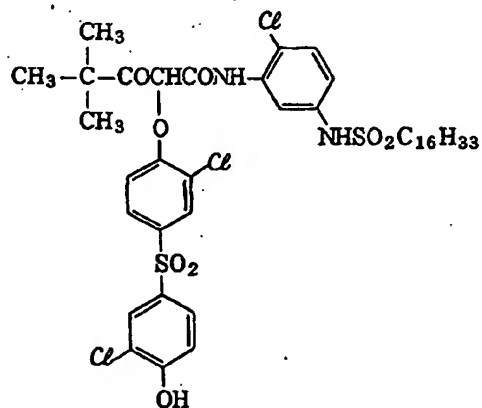
( Y - 3 5 )



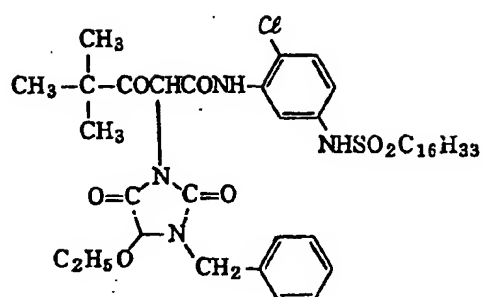
( Y - 3 6 )



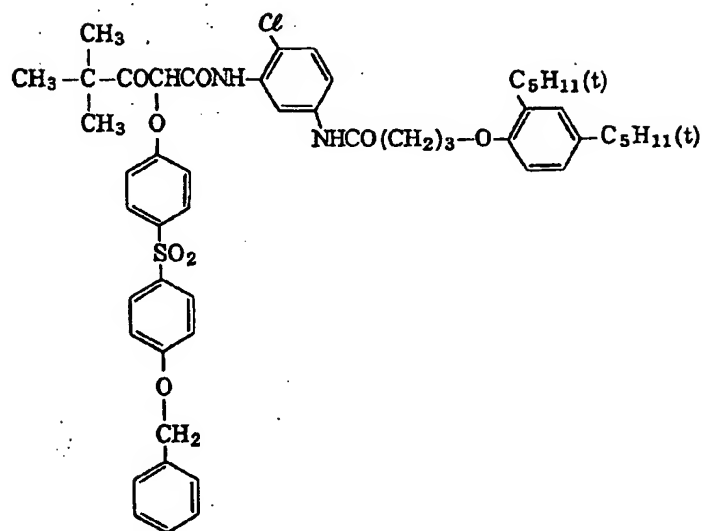
( Y - 3 7 )



( Y - 3 8 )

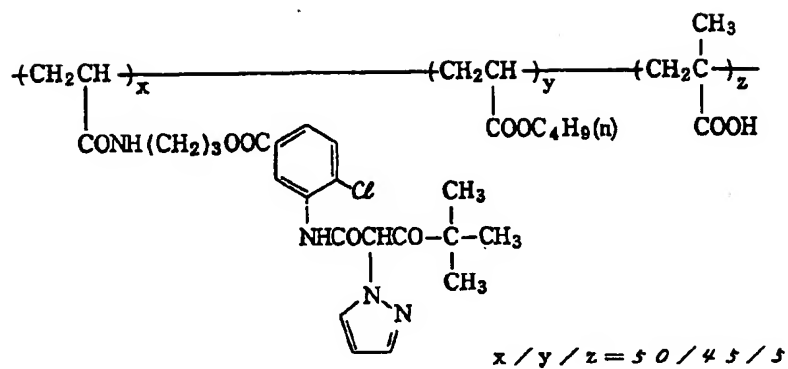


( Y - 3 9 )



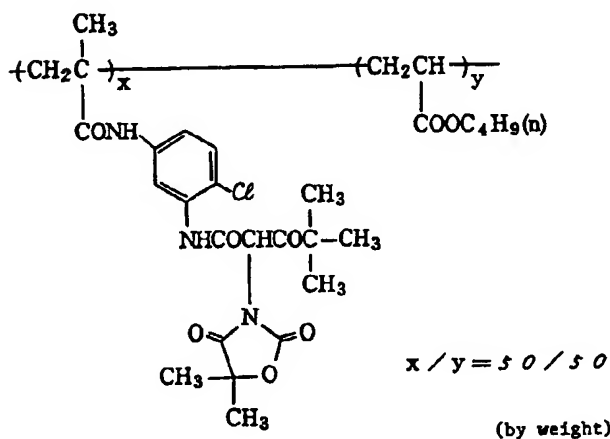


( Y - 4 2 )

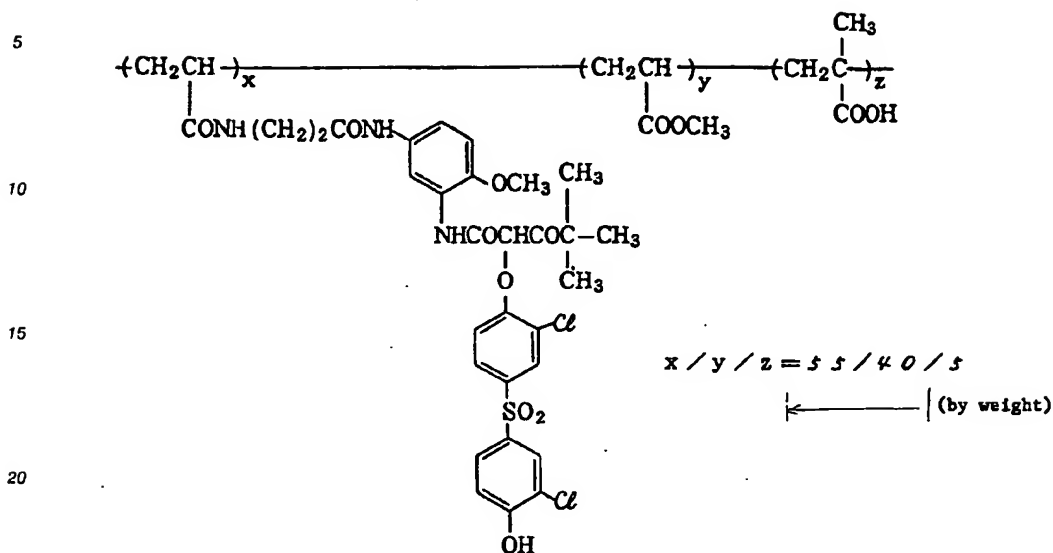


(by weight)

( Y - 4 3 )



( Y - 44 )

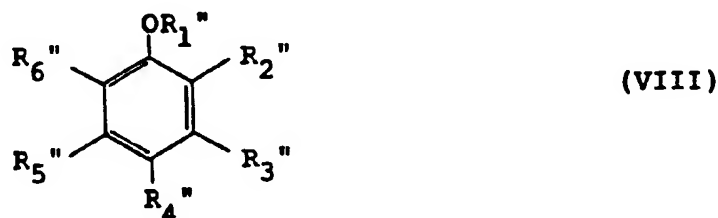


Application (OPI) No. 162548/84, U.S. Patent 3,725,067, Japanese Patent Application (OPI) Nos. 171956/84 and 33552/85.

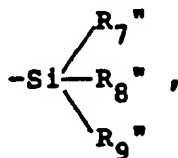
The yellow couplers of the formula (VII) can be synthesized by the methods described in Japanese Patent Application (OPI) No. 48541/79, Japanese Patent Publication No. 10739/83, U.S. Patent 4,326,024, Research Disclosure, RD No. 18053.

These couplers are generally added to emulsions in an amount of from  $2 \times 10^{-3}$  mol to  $5 \times 10^{-1}$  mol, preferably from  $1 \times 10^{-2}$  mol to  $5 \times 10^{-2}$  mol, per mol of the silver in the emulsion layer.

The compounds used in the present invention can be used together with known anti-fading agents, and especially preferred anti-fading agents are (i) aromatic compounds represented by the following formula (VIII), (ii) amino compounds represented by the following formula (IX), or (iii) metal complexes comprising a center atom of copper, cobalt, nickel, palladium or platinum and at least one organic ligand having two or more conformations.



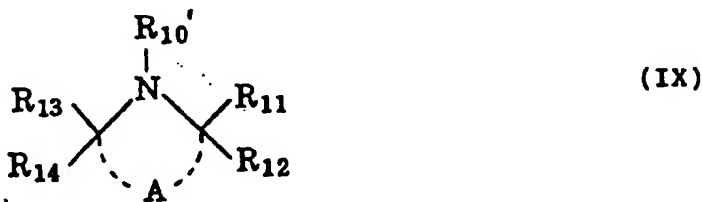
In the formula,  $R_1''$  represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group or a group of



in which  $R_7''$ ,  $R_8''$  and  $R_9''$  may be the same or different and each represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an alkenoxy group or an aryloxy group;

$R_2''$ ,  $R_3''$ ,  $R_4''$ ,  $R_5''$  and  $R_6''$  may be the same or different and each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acylamino group, an alkylamino group, an alkylthio group, an arylthio group, an alkoxy carbonyl group, an aryloxy carbonyl group, a halogen atom or  $-O-R_1''$ , in which  $R_1''$  has the same meaning as  $R_1''$ ;

or  $R_1''$  and  $R_2''$  may be bonded together to form a 5-membered ring, a 6-membered ring or a spiro ring; or  $R_2''$  and  $R_3''$ , or  $R_3''$  and  $R_4''$  may be bonded together to form a 5-membered ring, a 6-membered ring or a spiro ring.



In the formula,  $R_{10}'$  represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an acyl group, a sulfonyl group, a sulfinyl group, an oxy-radical or a hydroxyl group;  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$

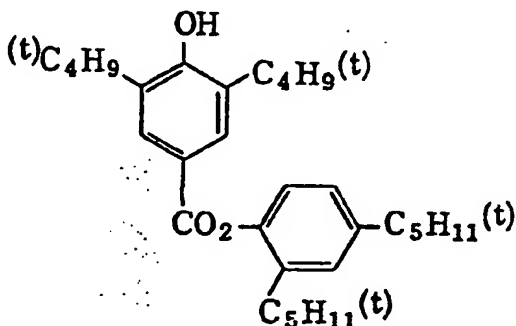


may be the same or different and each represents a hydrogen atom or an alkyl group; and A represents a non-metallic atomic group necessary for forming a 5-membered, 6-membered or 7-membered ring.

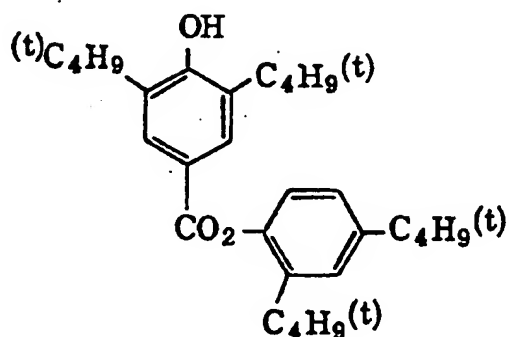
In the substituents in the formulae (VIII) and (IX), those containing, even in part, an alkyl group, an aryl group or a heterocyclic group can further be substituted by substituent(s).

5 The typical examples of the substituents in the formulae (VIII) and (IX) are those described in Japanese Patent Application (OPI) No. 92945/87, pages 12 and 13, and the specific examples of the compounds of these formulae are the compound Nos. (A-1) through (A-60) described in Japanese Patent Application (OPI) No. 92945/87, pages 13 to 17 and additionally the following compounds.

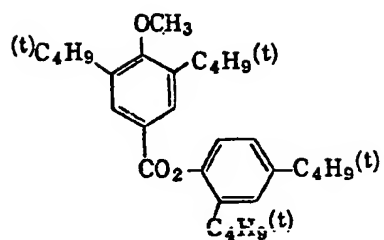
10 A - 6 1



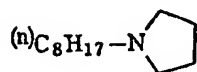
30 A - 6 2



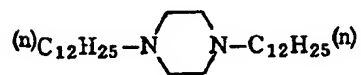
A - 6 3



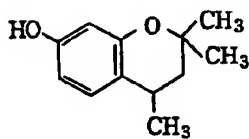
A - 6 4



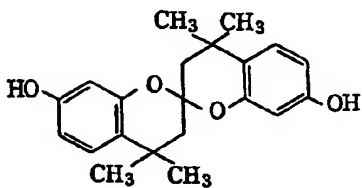
A - 6 5



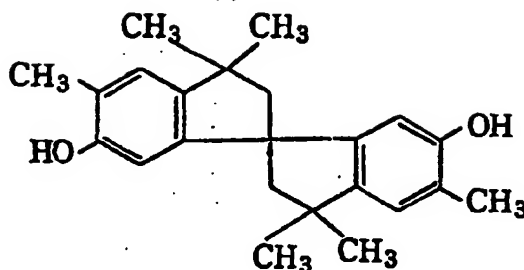
A - 6 6



A - 6 7



A - 6 8



A - 6 9



The amount of the compound of the formulae (VIII) and (IX) to be added is from 10 to 400 mol%, preferably from 30 to 300 mol%, to the coupler. On the other hand, the amount of the metal complex to be added is from 1 to 100 mol%, preferably from 3 to 40 mol%, to the coupler.

In the photographic materials prepared, if the hydrophilic colloid layers contain a dye or an ultraviolet absorbent, these can be mordanted by a cationic polymer.

The photographic materials prepared can contain, as a color-fog inhibitor, a hydroquinone derivative, an aminophenol derivative, a gallic acid derivative or a ascorbic acid derivative.

The photographic materials prepared can contain an ultraviolet absorbent in the hydrophilic colloid layer. For instance, aryl group-substituted benzotriazole compounds (for example, as described in U.S. Patent 3,533,794), 4-thiazolidone compounds (for example, as described in U.S. Patents 3,314,794 and 3,352,681), benzophenone compounds (for example, as described in Japanese Patent Application (OPI) No. 2784/71), cinnamic acid ester compounds (for example, as described in U.S. Patents 3,705,805 and 3,707,375), butadiene compounds (for example, as described in U.S. Patent 4,045,229) or benzoxazole compounds (for example, as described in U.S. Patent 3,700,455) can be used. Ultraviolet-absorbing couplers (for example,  $\alpha$ -naphthol series cyan dye-forming couplers and ultraviolet-absorbing polymers may also be used. These ultraviolet absorbents can be mordanted in specifically determined layers.

The photographic materials can contain a water-soluble dye in the hydrophilic colloid layer as a filter dye or for the purpose of irradiation prevention or for any other various purposes. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. In particular, oxonol dyes, hemioxonol dyes and merocyanine dyes are especially useful.

As the binder or protective colloid which can be used for the emulsion layers of the photographic materials, gelatin is advantageously used, but other hydrophilic colloids can also be used singly or together with gelatin.

As gelatin, lime-processed gelatin as well as acid-processed gelatin can be used in the photographic materials. The details of the method for the preparation of gelatins is described in Arthur Veis, The Macromolecular Chemistry of Gelatin (by Academic Press, 1964).

In the photographic emulsion layers of the photographic light-sensitive materials to be used in the present invention, any of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide and silver chloride can be used as a silver halide.

The mean grain size (the diameter of the grain when the grain has a spherical shape or resembles a spherical shape, or the mean value based on the projected area using the edge length as the grain size when the grain is a cubic shaped grain) of the silver halide grains in the photographic emulsions is not specifically limitative but is preferably 2  $\mu\text{m}$  or less.

The grain size distribution of the silver halide emulsions may be narrow or broad, but a so-called monodispersed emulsion wherein the fluctuation value is 15% or less is preferably used in the present invention.

The silver halide grains in the photographic emulsions may have a regular crystal form such as cubic or

octahedral or an irregular crystal form such as spherical or tabular, or further a composite form of these crystal forms. Also, the emulsions may be a mixture comprising grains of various crystal forms. In particular, the use of normal crystal grains is preferred.

In addition, a tabular grain silver halide emulsion wherein tabular silver halide grains having an aspect ratio (length/width) of 5 or more account for 50% or more of the total projected area of the silver halide grains may also be used.

The silver halide grains may have a different inner phase and surface layer phase. In addition, these may be of a surface latent image type capable of forming latent images mainly on the surface thereof or of an interanal latent image type capable of forming latent images mainly in the inside thereof.

The silver halide grains may also be formed, or physically ripened, in the presence of a cadmium salt, a zinc salt, a thallium salt, a lead salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, an iron salt or a complex salt thereof.

The silver halide emulsions are generally subjected to chemical sensitization.

The photographic emulsions for use in the photographic materials of the present invention can contain various compounds so as to prevent the generation of fog in the manufacture step of the materials or during the storage or photographic processing of the materials or so as to stabilize the photographic characteristics of the materials. For example, various kinds of compounds which are known as an antifoggant or stabilizer can be added to the emulsions, and examples of such compounds are azoles, such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole), mercaptopyrimidines, mercaptotriazines,; thioketo compounds such as oxazolinethiones,; azaindenes such as triazaindenes, tetrazaindenes (especially 4-hydroxy-substituted (1,3,3a,7)tetrazaindenes), pentazaindenes, etc.; benzenethiosulfonic acids, benzenesulfinic acids, benzenesulfonic acid amides.

The present invention can be applied to multi-layer and multi-color photographic materials having at least two emulsion layers of different spectral sensitivities on a support. Multi-layer natural color photographic materials generally have at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer on a support. The disposition order of these emulsion layers can be selected according to the intended use. In general, the red-sensitive emulsion layer contains a cyan-forming coupler, the green-sensitive emulsion layer contains a magenta-forming coupler, and the blue-sensitive emulsion layer contains yellow-forming coupler, but as the case may be, different combinations can be used.

As the supports for use in the present invention, conventional ones which are generally used in photographic materials can be used, including cellulose nitrate film, cellulose acetate film, cellulose acetate-butyrate film, cellulose acetate-propionate film, polystyrene film, polyethylene terephthalate film, polycarbonate film, as well as laminates comprising the said films, thin glass film, paper,. In addition, papers coated or laminated with baryta or an  $\alpha$ -olefin polymer, especially a polymer of an  $\alpha$ -olefin having from 2 to 10 carbon atoms, such as polyethylene, polypropylene or ethylene-butene copolymer, as well as plastic film supports whose surface is roughened so as to improve the adhesiveness with other high molecular substances, as described in Japanese Patent Publication No. 19068/72, are usable in the present invention, and these supports can yield a good result. Further, ultraviolet-setting resins can also be used.

As the support, transparent or opaque ones are selectively used in accordance with the intended object of the photographic materials. In addition, dyes or pigments can be added to the supports so as to make them transparently colored.

Opaque supports include, in addition to naturally opaque supports such as paper, those formed by adding a dye or a pigment such as titanium oxide to a transparent film; as well as surface-processed plastic films as described in Japanese Patent Publication No. 19068/72; and completely light-shielding papers or plastics to which a carbon black, or a dye is added. The support generally has a subbing layer. In order to further improve the adhesiveness, the surface of the support can be pre-treated, for example, by corona discharge, ultraviolet irradiation or flame-treatment.

As the color photographic materials to be used for preparing the color photographs of the present invention, conventional color photographic materials can be used, and in particular, color photographic materials for prints are especially preferred. Further, photographic materials to be processed by the color photographic process described in U.S. Patents 3,227,550, 3,227,551 and 3,227,552 and Temporarily Published U.S. Patent U.S. B. 351,673, etc.; in particular those to be processed by a color diffusion transfer photographic process, can also be used. In order to obtain color images by conventional photographic processing, the color photographic materials are required to be subjected to color photographic development processing, after being exposed. The color photographic development processing basically comprises

a color development step, a bleaching step and a fixation step. The two steps of bleaching and fixation can be carried out in one operation. Alternatively, a combination comprising color development, first fixation and then bleaching-fixation is also possible. The development step is optionally combined with various steps of pre-hardening, neutralization, first development (black-and-white development), image stabilization, rinsing, if desired. The processing temperature is generally 18°C or higher. Especially, the temperature is from 20°C to 60°C in most cases, and recently, the temperature is within the range of from 30°C to 60°C.

The color developer is an aqueous alkaline solution containing an aromatic primary amine series color developing agent and having a pH value of 8 or more, preferably from 9 to 12.

After the step of fixation or bleaching-fixation, the photographic materials are generally subjected to rinsing in water. However, in place of the rinsing step in water, a simple step of only a so-called "stabilization" can also be effected with no substantial rinsing operation.

Preferred examples of aromatic primary amine series developing agents for use in the present invention are p-phenylenediamine derivatives, and specific examples thereof are set forth hereunder, which, however, are not limitative.

- 15 D-1: N,N-diethyl-p-phenylenediamine
- D-2: 2-Amino-5-diethylaminotoluene
- D-3: 2-Amino-5-(N-ethyl-N-laurylamino)toluene
- D-4: 4-[N-ethyl-N-( $\beta$ -hydroxyethyl)amino]aniline
- D-5: 2-Methyl-4-[N-ethyl-N-( $\beta$ -hydroxyethyl)amino]- aniline
- 20 D-6: N-Ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl- 4-aminoaniline
- D-7: N-(2-amino-5-diethylaminophenylethyl)methane- sulfonamide
- D-8: N,N-dimethyl-p-phenylenediamine
- D-9: 4-Amino-3-methyl-N-methoxyethylaniline
- D-10: 4-Amino-3-methyl-N-ethyl-N- $\beta$ -ethoxyethylaniline
- 25 D-11: 4-Amino-3-methyl-N-ethyl-N- $\beta$ -butoxyethylaniline

These p-phenylenediamine derivatives may also be in the form of salts such as sulfates, hydrochlorides, sulfites, p-toluenesulfonates,. The above-mentioned compounds are described in U.S. Patents 2,193,015, 2,552,241, 2,566,271, 2,592,364, 3,656,950 and 3,698,525. The concentration of the aromatic amine developing agent to be used in actual processing is from 0.1 g to 20 g, more preferably from 0.5 g to 10 g, per liter of the developer bath solution.

The color developer for use in the present invention can contain hydroxylamines, as are well known.

The processing temperature of the color developer in the practice of the present invention is preferably from 30°C to 50°C, more preferably from 33°C to 42°C. The amount of the replenisher in the color development step is from 30 ml to 2000 ml, preferably from 30 ml to 1500 ml, per m<sup>2</sup> of the photographic materials being processed. In view of the necessity for reducing the amount of wastes, a small amount of the replenisher is better.

If the color developer contains benzyl alcohol, the amount of the benzyl alcohol is preferably 2.0 ml/liter or less, more preferably 0.5 ml/liter or less. No benzyl alcohol is most preferred. The color development time is preferably within 2 minutes and 30 seconds or less, more preferably within the range of from 10 seconds to 2 minutes and 30 seconds. The most preferred range is from 45 seconds to 2 minutes.

The following examples are intended to illustrate the present invention but not to limit it in any way.

Unless otherwise specified, all percents, ratios, are by weight.

#### EXAMPLE 1

45 5 g of a dye obtained by oxidation-coupling reaction of the above-mentioned Cyan Coupler (C-1) and 4-amino-3-methyl-N-ethyl-N- $\beta$ -(methanesulfonamido)ethylaniline (the dye is referred to as Dye (C-1), and the same shall apply hereinafter with respect to the naming of dyes) was dissolved in 20 ml of trisresyl phosphate and 20 ml of ethyl acetate, and the resulting solution was emulsified and dispersed in 80 g of a gelatin solution containing 8 ml of aqueous 1%-sodium dodecylbenzenesulfonate solution.

Next, sodium dodecylbenzenesulfonate was added to the emulsified dispersion as a coating auxiliary agent and then coated on a paper support both surfaces of which had been laminated with polyethylene.

The amount of the dye coated was so controlled that the color density as measured with Macbeth Densitometer RD-514 Type (Status AA Filter) was 1.0.

55 A gelatin protective layer (containing 1 g/m<sup>2</sup> of gelatin) was coated over the layer, to obtain Sample (A).

In the same manner as above, other Samples (A-1) through Samples (A-13) were manufactured, using the combinations as shown in the following Table 1 in the preparation of the respective emulsified dispersions.

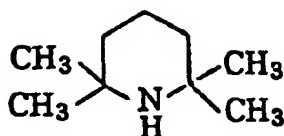
The samples thus obtained were stored in the dark at room temperature for 2 months. In order to test the light-fastness of each sample, the samples were subjected to a color fading test for 500 hours with a xenon tester (illuminance: 100,000 luxes) provided with an ultraviolet absorbing filter (by Fuji Photo Film) cutting a light of 400 nm or less, and the color retention (percentage) was obtained for each sample. The results are set forth in Table 1.

Table 1

Sample	Dye	Amount of 4-Amino-3-methyl-N-ethyl-N-β-(methanesulfonylamido)ethylaniline $\frac{3}{2} \text{H}_2\text{SO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ added (mol% to dye)	Additive (Amount added, mol% to dye)	Color Retention (%)	Note
A	(C-1) Dye	-	-	56	Comparative Sample
A-1	"	20	-	40	"
A-2	"	"	(I - 1)	50	Sample of the Invention
A-3	"	"	(I - 5)	58	"
A-4	"	"	(I - 18)	57	"
A-5	"	"	(II - 1)	55	"
A-6	(C-14) Dye	-	-	34	Comparative Sample
A-7	"	20	-	23	"
A-8	"	"	(I - 3)	37	Sample of the Invention
A-9	"	"	(I - 10)	37	"
A-10	"	"	(II - 4)	35	"
A-11	"	"	(Comparative Compound A)	25	Comparative Sample
A-12	"	"	(Comparative Compound B)	26	"
A-13	"	"	(Comparative Compound C)	19	"

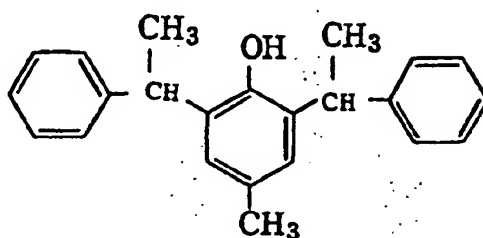
(Comparative Compound A)

Compound described in British Patent 1,326,889 as an anti-fading agent.



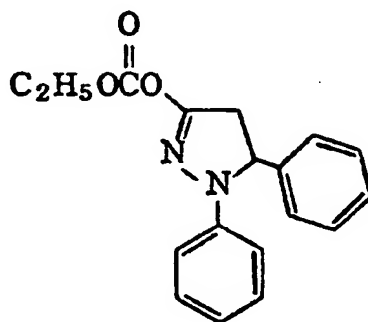
(Comparative Compound B)

Compound described in Japanese Patent Publication No. 30462/76.



(Comparative Compound C)

Compound described in Japanese Patent Application (OPI) No. 104641/84.



As is apparent from Table 1, the addition of the compound used in the present invention is effective for improving the fastness against the deterioration of the fastness caused by the developing agent remaining in the photographic material processed. The degree of the effect could not be anticipated from any known anti-fading agents.

## EXAMPLE 2

In the same manner as Example 1, except that the Dye (C-1) in the Sample (A) was replaced by a dye obtained by oxidation-coupling reaction of the Magenta Coupler (M-1) and 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline, Sample (B) was prepared. In addition, Samples (B-1) through (B-26) were also prepared, using the combinations as shown in Table 2.

These samples were stored for 2 months in the dark in the same manner as in Example 1. These were subjected to a color-fading test with a xenon tester for 200 hours, and the color retention (percentage) was obtained for each sample. The results are set forth in Table 2.

Table 2

Sample	Dye	Amount of 4-Amino-3-methyl-N-ethyl-N-6-(methanesulfonamido)ethylaniline 3/2 H <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O added (mols to dye)	Additive (Amount added, mol% to dye)	Color Retention (%)	Note
B	(M-1) Dye	-	-	49	Comparative Sample
B-1	"	20	-	21	"
B-2	"	"	(I - 2)	47	Sample of the Invention
B-3	"	"	(I - 6)	46	"
B-4	"	"	(I - 13)	51	"
B-5	"	"	(Comparative Compound A)	22	Comparative Sample
B-6	"	"	(Comparative Compound B)	27	"
B-7	(M-6) Dye	-	-	47	"
B-8	"	20	-	25	"
B-9	"	"	(I - 1)	46	Sample of the Invention
B-10	"	"	(II - 2)	43	"

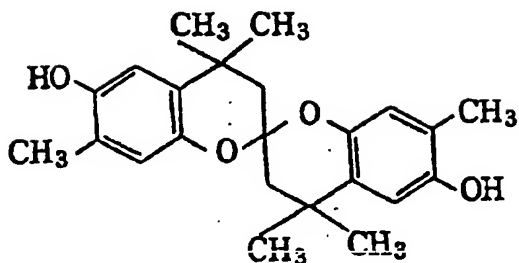


Table 2 (continued)

Sample	Dye	Amount of 4-Amino-3-methyl-N-ethyl-N-β-(methanesulfonylamido)ethylaniline 3/2 H <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O added (mole to dye)	Additive (Amount added, mol% to dye)	Color Retention (%)	Note
B-11	(M-16) Dye	-	-	39	Comparative Sample
B-12	"	20	-	22	"
B-13	"	"	(I - 3)	50	Sample of the Invention
B-14	"	"	(I - 5)	50	"
B-15	"	"	(I - 16)	50	"
B-16	"	"	(II - 1)	50	"
B-17	"	"	(II - 4)	50	"
B-18	(M-31) Dye	-	-	45	Comparative Sample
B-19	"	20	-	23	"
B-20	"	"	(I - 1)	50	Sample of the Invention
B-21	"	"	(I - 11)	50	"
B-22	"	"	(I - 22)	50	"
B-23	"	"	(II - 4)	50	"
B-24	"	"	(Comparative Compound D)	50	Comparative Sample
B-25	"	"	(Comparative Compound E)	50	"
B-26	"	"	(Comparative Compound F)	50	"

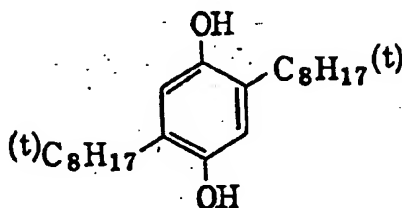
(Comparative Compound D)

Compound described in U.S. Patent 3,764,337



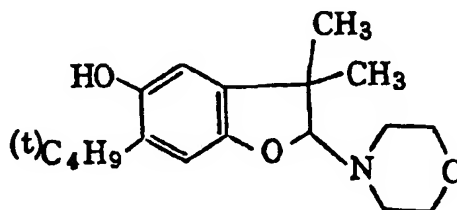
(Comparative Compound E)

Compound described in U.S. Patent 3,930,866



(Comparative Compound F)

Compound described in U.S. Patent 3,573,050



As is apparent from Table 2, the compounds used in the present invention are extremely effective for preventing the deterioration of image quality caused by developing agents, although the fastness of images is deteriorated because of the existence of the developing agents remaining in the photographic materials. The effect could not be anticipated from any known compounds.

### EXAMPLE 3

In the same manner as in Example 1, except that the Dye (C-1) in the Sample (A) was replaced by a dye obtained by a coupling reaction of the Yellow Coupler (Y-35) and 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline, Sample (C) was prepared. In addition, Samples (C-1) through Samples (C-12) were also prepared, using the combinations as shown in Table 3.

These samples were stored for 2 months in the dark in the same manner as in Example 1. In order to test the light-fastness of each sample, these samples were subjected to a color-fading test in the same manner as in Example 1 with a xenon tester for 800 hours. In addition, in order to test the heat-resistance of each sample, the samples were stored in the dark for 500 hours at 100°C. The results of the color retention (percentage) of each sample are shown in Table 3.

Table 3

Sample	Dye	Amount of 4-Amino-3-methyl-N-ethyl-N-β-(methanesulfonylamido)ethylaniline 3/2 H <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O added (mols to dye)	Additive (Amount added, mols to dye)	Color Retion (%)		Note
				Xe light (for 800 hours)	100°C (for 500 hours)	
C	(Y-35) Dye	-	-	65	89	Comparative Sample
C-1	"	20	-	56	81	"
C-2	"	"	(I - 15) 50	64	87	Sample of the Invention
C-3	"	"	(I - 22) 50	65	87	"
C-4	"	"	(I - 24) 50	65	88	"
C-5	"	"	(II - 1) 50	64	89	"
C-6	(Y-38) Dye	-	-	63	88	Comparative Sample
C-7	"	20	-	55	83	"
C-8	"	"	(I - 6) 50	63	87	Sample of the Invention
C-9	"	"	(I - 7) 50	63	88	"
C-10	"	"	(I - 9) 50	64	87	"
C-11	"	"	(Comparative Compound A) 50	54	85	Comparative Sample
C-12	"	"	(Comparative Compound B) 50	55	82	"

As apparent from Table 3, the addition of the compound used in the present invention is extremely effective for improving the fastness to light and heat, and the color fading caused by the developing agent was effectively prevented.

#### EXAMPLE 4

P-anisidine and the compound of the formula (I) of the present invention were dissolved in trinonyl phosphate each in a concentration of 0.03 mol/liter. 10 ml of the mixture was heated in a thermostatic bath at 80°C, whereupon the reaction was followed by high performance liquid chromatography to obtain the

secondary reaction rate constant.

The secondary reaction rate constants  $k_2$  of specific compounds thus obtained are shown in Table 4.

Table 4

Compound	$k_2$ (l/mol sec)	Compound	$k_2$ (l/mol sec)
(I - 1)	$5 \times 10^{-5}$	(I - 2)	$7.1 \times 10^{-1}$
(I - 3)	$9.76 \times 10^{-2}$	(I - 4)	$2.85 \times 10^{-3}$
(I - 6)	$5.77 \times 10^{-5}$	(I - 7)	$2 \times 10^{-5}$
(I - 8)	$3.83 \times 10^{-4}$	(I - 9)	$2 \times 10^{-5}$
(I - 13)	$3.34 \times 10^{-5}$	(I - 22)	$3.07 \times 10^{-4}$
(I - 25)	$7.16 \times 10^{-5}$	(I - 28)	$2.47 \times 10^{-3}$
(I - 31)	$2.37 \times 10^{-3}$	(I - 35)	$5.63 \times 10^{-3}$
(I - 36)	$1.09 \times 10^{-2}$	(I - 40)	$1.93 \times 10^{-3}$
(I - 43)	$5.95 \times 10^{-3}$	(I - 45)	$4.17 \times 10^{-3}$
(I - 49)	$1.46 \times 10^{-3}$	(I - 53)	$2.16 \times 10^{-4}$
(I - 57)	$1.76 \times 10^{-2}$	(I - 61)	$2.00 \times 10^{-2}$
(I - 67)	$1.57 \times 10^{-2}$	(I - 72)	$1.64 \times 10^{-2}$
(I - 77)	$8.95 \times 10^{-4}$	(I - 84)	$4.11 \times 10^{-3}$
(I - 85)	$9.61 \times 10^{-4}$	(I - 87)	$1.01 \times 10^{-3}$
(I - 91)	$2.56 \times 10^{-3}$	(I - 94)	$1.53 \times 10^{-3}$
(I - 97)	$2.15 \times 10^{-3}$	(I - 100)	$5.00 \times 10^{-4}$
(I - 108)	$1.61 \times 10^{-3}$	(I - 112)	$1.61 \times 10^{-3}$

#### EXAMPLE 5

Plural layers comprising the first layer (undermost layer) to the second layer (uppermost layer) as described below were coated in order on a paper support both surfaces of which had been laminated with polyethylene, to obtain a color photographic material sample.

The polyethylene-laminated paper support contained a white pigment (such as  $\text{TiO}_2$ ) and a bluish dye (such as ultramarine) in the polyethylene in the side of the first layer.

##### First Layer: Blue-sensitive Layer

Silver chlorobromide emulsion (silver bromide: 80 mol%)	0.35 g/m <sup>2</sup> as Ag
Gelatin	1.35 g/m <sup>2</sup>
Yellow coupler	$6.91 \times 10^{-4}$ mol/m <sup>2</sup>
Color image stabilizer (A-43)	0.13 g/m <sup>2</sup>
Solvent (a)	0.02 g/m <sup>2</sup>

##### Second Layer: Color Mixing Preventing Layer

Gelatin	0.90 g/m <sup>2</sup>
Color mixing preventing agent (b)	$2.33 \times 10^{-4}$ mol/m <sup>2</sup>

Third Layer: Green-sensitive Layer	
Silver Chlorobromide emulsion (silver bromide: 75 mol%)	0.15 g/m <sup>2</sup> as Ag
Gelatin	1.56 g/m <sup>2</sup>
Magenta coupler	3.38x10 <sup>-4</sup> mol/m <sup>2</sup>
Color image stabilizer (A-18)	0.19 g/m <sup>2</sup>
Solvent (c)	0.59 g/m <sup>2</sup>

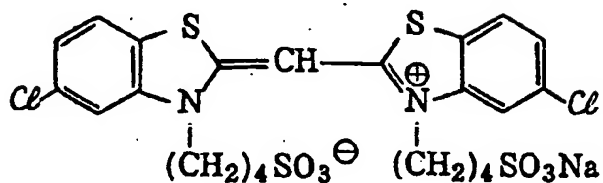
Fourth Layer: Ultraviolet Absorbing Layer	
Gelatin	1.60 g/m <sup>2</sup>
Ultraviolet absorbent (d)	1.70x10 <sup>-4</sup> mol/m <sup>2</sup>
Color mixing preventing agent (A-30)	1.60x10 <sup>-4</sup> mol/m <sup>2</sup>
Solvent (a)	0.24 g/m <sup>2</sup>

Fifth Layer: Red-sensitive Layer	
Silver chlorobromide emulsion (silver bromide: 70 mol%)	0.22 g/m <sup>2</sup> as Ag
Gelatin	0.90 g/m <sup>2</sup>
Cyan coupler	7.05x10 <sup>-4</sup> mol/m <sup>2</sup>
Color image stabilizer (f)	5.20x10 <sup>-4</sup> mol/m <sup>2</sup>
Solvent (e)	0.6 g/m <sup>2</sup>

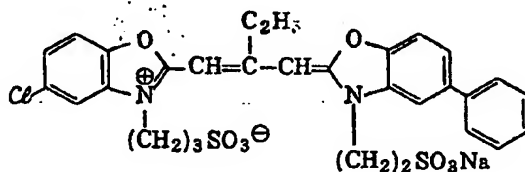
Sixth Layer: Ultraviolet Absorbing Layer	
Gelatin	0.54 g/m <sup>2</sup>
Ultraviolet absorbent (d)	5.10x10 <sup>-4</sup> mol/m <sup>2</sup>
Solvent (a)	0.08 g/m <sup>2</sup>

Seventh Layer: Protective Layer	
Gelatin	1.33 g/m <sup>2</sup>
Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17%)	0.17 g/m <sup>2</sup>

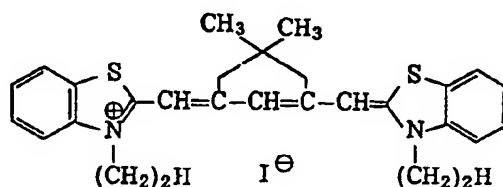
As the spectral sensitizer for the respective emulsions, the following dyes were used.

Blue-sensitive Emulsion Layer:

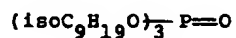
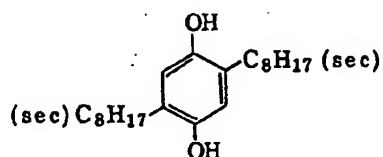
(Amount added:  $2 \times 10^{-4}$  mol per mol of silver halide)

Green-sensitive Emulsion Layer:

(Amount added:  $2.5 \times 10^{-4}$  mol per mol of silver halide)

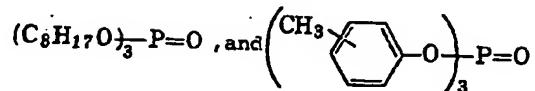
Red-sensitive Emulsion Layer

(Amount added:  $2.5 \times 10^{-4}$  mol per mol of silver halide)

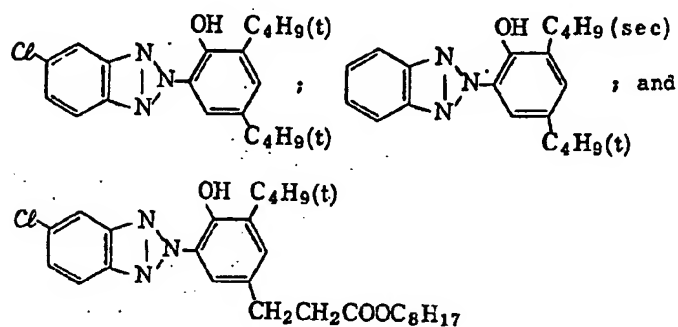
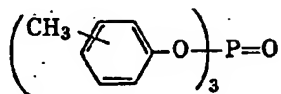
Solvent (a):Color Mixing Preventing Agent (b):

Solvent (c)

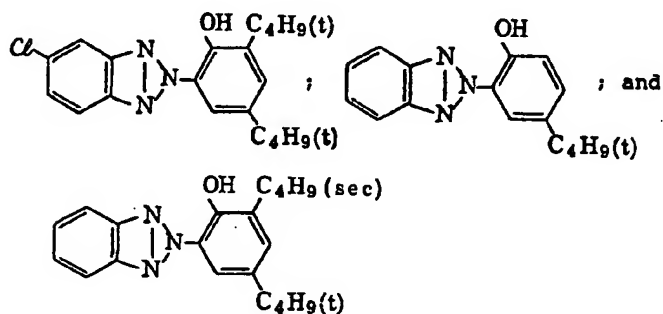
Mixture (2/1 by weight) of the following compounds

Ultraviolet Absorbent (d):

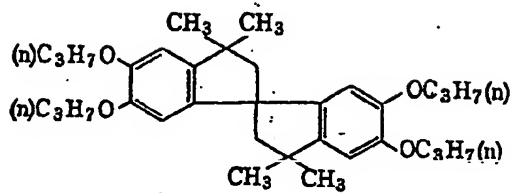
Mixture (1/5/3 by mol) of the following compounds

Solvent (e):Color Image Stabilizer (f):

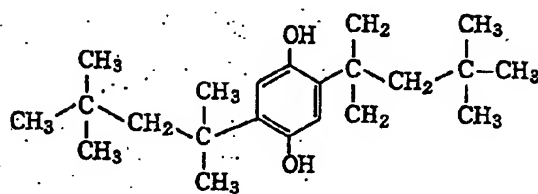
Mixture (1/3/3 by mol) of the following compounds



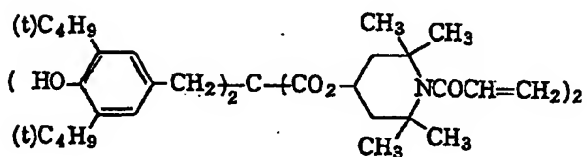
A - 1 8



A - 3 0

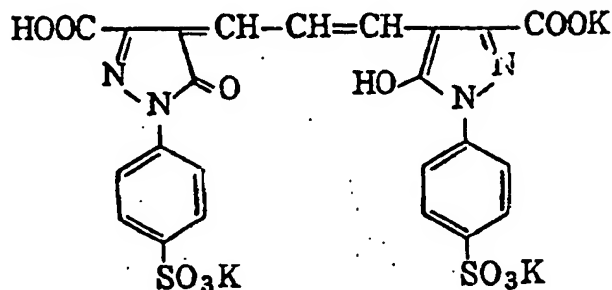


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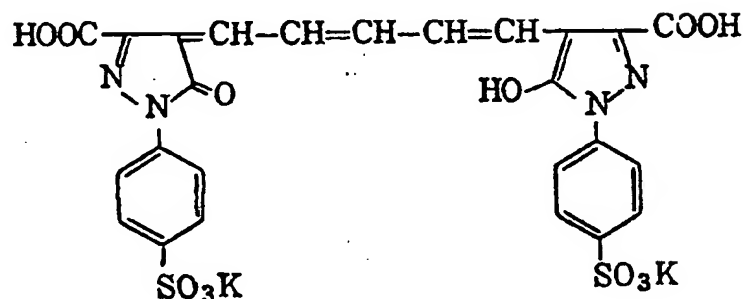


As the anti-irradiation dye for the respective layers, the following dyes were used.





### Red-sensitive Emulsion Layer



Next, the samples thus prepared were exposed to light through an optical wedge and then processed in accordance with the following process (A) or (B) to form color images in the respective samples.

**Process (A):**

The samples exposed were subjected to running development with Fuji Color Roll Processor FMPP 1000 (partly modified) (by Fuji Photo Film Co.) under the conditions described below.

Step	Time (seconds)	Temperature	Tank Capacity (liter)	Amount of Replenisher (ml/m <sup>2</sup> )
Color Development	45	35 ° C	88	150
Bleach-fixation	45	35 ° C	35	50
Rinsing (1)	20	35 ° C	17	-
Rinsing (2)	20	35 ° C	17	-
Rinsing (3)	20	35 ° C	17	250

The rinsing step was carried out by means of a three tank-countercurrent system, where a replenisher

was replenished into the rinsing tank (3), the solution overflowed from the rinsing tank (3) was introduced into the bottom of the rinsing tank (2), the solution overflowed from the rinsing tank (2) was introduced into the bottom of the rinsing tank (1), and the solution overflowed from the rinsing tank (1) was drained out therefrom. The amount of the processing solution as taken out from the previous bath into the next bath together with the photographic paper being processed in this system was 25 ml per m<sup>2</sup> of the paper.

The processing solutions in the respective tanks and the replenishers had the following compositions:

Color Developer:		
	Tank Solution	Replenisher
Water	800 ml	800 ml
Diethylenetriamine-pentaacetic acid	3.0 g	3.0 g
Benzyl alcohol	15 ml	17 ml
Diethylene glycol	10 ml	10 ml
Sodium sulfite	2.0 g	2.5 g
Potassium bromide	0.5 g	-
Sodium carbonate	30 g	35 g
N-Ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	7.0 g
Hydroxylamine sulfate	4.0 g	4.5 g
Brightening agent	1.0 g	1.5 g
Water to make	1000 ml	1000 ml
pH	10.10	10.50

Bleaching-fixation Solution:		
	Tank Solution	Replenisher
Water	400 ml	400 ml
Ammonium thiosulfate (70 wt%)	150 ml	300 ml
Sodium sulfite	12 g	25 g
Ammonium ethylenediamine-tetraacetic acid iron (III)	55 g	110 g
2Na Ethylenediamine-tetraacetate	5 g	10 g
Water to make	1000 ml	1000 ml
pH (25 ° C)	6.70	6.50

Rinsing Solution:	
Ethylenediamine-N,N,N',N'-tetramethylenephosphonate	0.3 g
Benzotriazole	1.0 g
Water to make	1000 ml
Sodium hydroxide to make	pH 7.5

Process (B):

Step	Time	Temperature	Tank Capacity (liter)	Amount of Replenisher (ml/m <sup>2</sup> )
Color Development	45 sec	35 °C	88	150
Bleach-fixation	2 min	35 °C	35	350
Rinsing (1)	1 min	35 °C	17	-
Rinsing (2)	1 min	35 °C	17	-
Rinsing (3)	1 min	35 °C	17	1300

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The processing solutions and the replenishers were same as those used in the process (A).

Next, the yellow reflection density in the non-image part of each of the samples as processed by the above-mentioned process was measured after one hour from the processing. In addition, after being left at 80 °C (10 to 15% RH) for 7 days or after being left at 80 °C (70% RH) for 8 days, the yellow reflection density in the non-image part of each sample was also measured. The results are shown in the following Table 5.

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Table 5

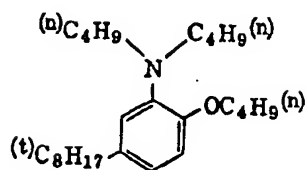
Sample	Yellow Coupler	Additive	Amount Added (mol% to Coupler)	Process	Increment of Yellow Stain		Notes
					80°C, 7 Days	80°C/70% RH, 8 Days	
D	Y-35	-	-	A	0.04	0.11	Comparison
D	"	-	-	B	0.01	0.01	"
D-1	"	I - 1	30	A	0.01	0.02	Invention
D-2	"	I - 3	"	A	0.01	0.02	"
D-3	"	I - 5	"	A	0.00	0.03	"
D-4	"	I - 7	"	A	0.01	0.02	"
D-5	"	I - 12	"	A	0.01	0.03	"
D-6	"	I - 17	"	A	0.01	0.02	"
D-7	"	II - 1	50	A	0.00	0.02	"
D-8	"	Comparative Compound (G)	"	A	0.04	0.10	Comparison
D-9	"	Comparative Compound (H)	"	A	0.05	0.11	"
D-10	"	Comparative Compound (I)	"	A	0.04	0.11	"
D-11	"	Comparative Compound (J)	"	A	0.04	0.12	"

Table 5 (continued)

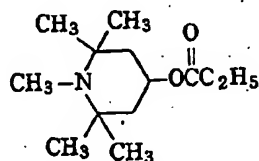
Sample	Yellow Coupler	Additive	Amount Added (mol% to Coupler)	Process	Increment of Yellow Stain 80°C/70% RH,		Notes
					80°C, 7 Days	8 Days	
D-12	Y-10	-	-	A	0.06	0.15	"
	"	-	-	B	0.01	0.09	"
D-13	"	I - 2	30	A	0.01	0.03	Invention
D-14	"	I - 6	"	A	0.02	0.03	"
D-15	"	I - 14	"	A	0.01	0.02	"
D-16	Y-36	-	-	A	0.05	0.10	Comparison
	"	-	-	B	0.01	0.01	"
D-17	"	I - 15	30	A	0.01	0.02	Invention
D-18	"	I - 16	"	A	0.00	0.01	"
D-19	"	Comparative Compound (D)	"	A	0.05	0.12	Comparison
D-20	"	Comparative Compound (E)	"	A	0.05	0.09	"
D-21	"	I - 61	20	A	0.01	0.02	Invention
D-22	"	I - 67	"	A	0.01	0.01	"
D-23	"	I - 85	"	A	0.01	0.02	"
D-24	"	I - 87	"	A	0.01	0.01	"
D-25	"	I - 110	"	A	0.01	0.01	"

Comparative Compound (G):

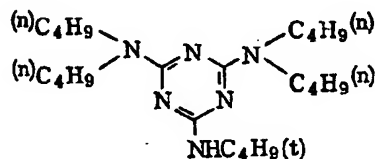
Compound described in U.S. Patent 4,483,918



Comparative Compound (H):  
Compound described in U.S. patent 4,463,085



Comparative Compound (I):  
Compound described in Japanese Patent Application (OPI) No. 218445/84



Comparative Compound (J):

Compound described in Japanese Patent Application (OPI) No. 229557/84

$\text{C}_{12}\text{H}_{23}\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$

Table 5 indicates that in the process B where the rinsing and bleach-fixing time was long and the amount of the replenisher in the respective processing steps was sufficient, there occurred no problem of yellow stain in the samples processed, while in the process A where the processing time was short and the amount of replenisher was small, the samples processed had noticeable yellow stain. Even under such circumstances, the yellow stain was sufficiently prevented by the addition of the compound used in the present invention.

On the contrary, the addition of the comparative compounds which were used in conventional means was quite ineffective for prevention of the yellow stain.

#### EXAMPLE 6

In the same manner as Example 5, the plural layers as mentioned in Example 5 were coated in order on a paper support both surfaces of which had been laminated with polyethylene to prepare color photographic material samples.

Specifically, the yellow coupler and the magenta coupler were removed from the first layer and the fifth layer, respectively, and the above-mentioned Compound (M-28) was used as the magenta coupler in the third layer, to obtain Sample (E). Further, Sample (E-1) through Sample (E-28) were also prepared in the

same manner as the preparation of Sample (E), except that the combination of the magenta coupler and the compound used in the invention as shown in the following Table 6 was used.

The samples thus prepared were exposed to light through an optical wedge and then processed for color development in accordance with the following process where the developing agent and other processing solutions used were so constituted that they would easily remain in the photographic samples processed to form stains thereon, especially for the purpose of clearly demonstrating the effect of the present invention.

Step	Temperature	Time
Color Development	33 ° C	3 min 30 sec
Bleach-fixation	33 ° C	1 min 30 sec
Rinsing in water	20 to 25 ° C (without stirring)	1 min
Drying	50 to 80 ° C	2 min

The respective processing solutions had the following compositions:

Color Developer:	
3Na•nitritotriacetate	20 g
Benzyl alcohol	15 ml
Diethylene glycol	10 ml
Sodium sulfite	0.2 g
Potassium bromide	0.5 g
Hydroxylamine sulfate	3.0 g
4-Amino-3-methyl-N-ethyl-N-[ $\beta$ -methanesulfonamido]ethyl]-p-phenylenediamine sulfate	6.5 g
Sodium Carbonate (monohydrate)	30 g
Water to make	1000 ml
	(pH 10.1)

Bleach-fixing Solution:	
Above-mentioned color developer Ammonium thiosulfate (70 wt%) Sodium sulfite Sodium (EDTA)/Iron Disodium (EDTA) Water to make 1N Sulfuric acid to make	400 ml 150 ml 12 g 36 g 4 g 1000 ml pH 7.0
This solution was used after being aerated for 1 hour. (Note) The composition of the bleach-fixing solution was prepared on the presumption of such an inconvenient condition that the color developer adhered to the photographic material sample processed under a running state whereby a noticeable amount of the color developer was brought into the bleach-fixing solution together with the sample processed and hence the bleach-fixing solution composition was fatigued and deteriorated.	



Next, the magenta reflection density (stain) in the non-image part of each sample was measured with a green light by a Fuji-type Auto-densitometer, after one hour from the development. Further, the magenta reflection density (stain) in the non-image part of each sample was also measured, after the samples were  
5 left at 80° C (70% RH) for 3 days or were left at room temperature for 50 days. The results are set forth in Table 6, where the increment of the stain from that measured one hour after the color development is shown.

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Table 6

Sample	Magenta Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Magenta Density		Notes
				80°C/70% RH, 3 Days	Room Temp., 50 Days	
E	M-23	-	-	0.36	0.28	Comparison
E-1	"	I - 2	30	0.11	0.01	Invention
E-2	"	I - 5	"	0.12	0.02	"
E-3	"	I - 7	"	0.11	0.01	"
E-4	"	I - 10	"	0.09	0.01	"
E-5	"	I - 14	"	0.09	0.01	"
E-6	"	I - 24	"	0.10	0.02	"
E-7	"	II - 1	50	0.13	0.03	"
E-8	"	(Comparative Compound G)	"	0.32	0.26	Comparison
E-9	"	(Comparative Compound H)	"	0.33	0.26	"
E-10	"	(Comparative Compound I)	"	0.34	0.27	"
E-11	"	(Comparative Compound J)	"	0.34	0.25	"

Table 6 (continued)

Sample	Magenta Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Magenta Density 80°C/70% RH, Room Temp.,		Notes
				3 Days	50 Days	
E-12	M-19	-	-	0.35	0.25	Comparison
E-13	"	I - 1	30	0.10	0.02	Invention
E-14	"	I - 3	"	0.11	0.02	"
E-15	"	II - 1	50	0.13	0.04	"
E-16	M-33	-	-	0.27	0.21	Comparison
E-17	"	I - 4	30	0.06	0.02	Invention
E-18	"	I - 9	"	0.07	0.02	"
E-19	"	I - 13	"	0.06	0.01	"
E-20	M-13	-	-	0.16	0.10	Comparison
E-21	"	I - 17	30	0.08	0.03	Invention
E-22	"	(Comparative Compound E)	"	0.15	0.10	Comparison
E-23	"	(Comparative Compound F)	"	0.17	0.11	"
E-24	M-23	I - 61	20	0.05	0.01	Invention
E-25	"	I - 67	"	0.06	0.01	"
E-26	"	I - 85	"	0.07	0.01	"
E-27	"	I - 87	"	0.08	0.01	"
E-28	"	I - 110	"	0.06	0.01	"

Table 6 clearly indicates that the effect of preventing the generation of stains after storage by the use of the compounds used in the invention is remarkable as compared with the use of the conventional known comparative compounds.

#### EXAMPLE 7

In the same manner as Example 5, the plural layers as mentioned in Example 5 were coated in order

on a paper support both surfaces of which had been laminated with polyethylene to prepare color photographic material samples.

Specifically, the yellow coupler and the magenta coupler were removed from the first layer and the third layer, respectively, and the above-mentioned Compound (C-2) was used as the cyan coupler in the fifth layer, to obtain Sample (F). Further, Sample (F-1) through Sample (F-21) were also prepared in the same manner as the preparation of Sample (F), except that the combination of the cyan coupler and the compound used in the invention as shown in the following Table 7 was used.

The samples thus prepared were exposed to light and processed for color development in the same manner as Example 6. After being processed, the cyan reflection density in the non-image part of each sample was measured with a red light by a Fuji-Type Auto-Densitometer. Further, the cyan reflection density in the non-image part of each sample was also measured, after the samples were left at 80 °C (70% RH) for 3 days or were left at 80 °C (dry, 10 to 15% RH) for 5 days. The results are set forth in Table 7.

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Table 7

Sample	Cyan Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Cyan Density		Notes
				80°C, 5 days	80°C/70% RH 3 Days	
F	C-2	-	-	0.07	0.23	Comparison
F-1	"	I - 1	30	0.03	0.07	Invention
F-2	"	I - 5	"	0.03	0.08	"
F-3	"	I - 9	"	0.03	0.07	"
F-4	"	I - 13	"	0.04	0.08	"
F-5	"	I - 17	"	0.03	0.08	"
F-6	"	II - 1	50	0.04	0.09	"
F-7	"	Comparative Compound A	"	0.08	0.24	Comparison
F-8	"	Comparative Compound B	"	0.07	0.23	"
F-9	"	Comparative Compound G	"	0.07	0.24	"
F-10	"	Comparative Compound H	"	0.08	0.24	"

Table 7 (continued)

Sample	Cyan Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Cyan Density		Notes
				80°C, 5 days	80°C/70% RH 3 Days	
F-11	C-25	-	-	0.06	0.22	Comparison
F-12	"	I - 3	30	0.02	0.06	Invention
F-13	"	I - 10	"	0.02	0.07	"
F-14	C-35	-	-	0.10	0.30	Comparison
F-15	"	I - 4	30	0.03	0.07	Invention
F-16	"	I - 7	"	0.04	0.06	"
F-17	C-2	I - 61	20	0.02	0.03	"
F-18	"	I - 67	"	0.02	0.04	"
F-19	"	I - 85	"	0.03	0.05	"
F-20	"	I - 87	"	0.03	0.05	"
F-21	"	I - 110	"	0.02	0.03	"

Table 7 clearly indicates that the effect of preventing the generation of stains after storage by the use of the compounds used in the invention is remarkable, and the level of the effect is high which could not be attained by any conventional technical arts.

#### EXAMPLE 8

In the same manner as Example 5, the first to seventh layers were coated on a paper suport both surfaces of which has been laminated with polyethylene to prepare color photographic material samples.

Specifically, the above-mentioned Compound (Y-35) was used as the yellow coupler in the first layer, the above mentioned Compound (M-23) was used as the magenta coupler in the third layer, and a mixture  
 5 (1/1 by mol) of the above mentioned Compounds (C-2) and (C-14) was used as the cyan coupler in the fifth layer, to obtain Sample (G). Further, Samples (G-1) through (G-12) were also prepared in the same manner as the preparation of Sample (G), except that the combination of the magenta coupler and the compound used in the invention as shown in the following Table 8 was used.

These samples were exposed to light through an optical wedge and the processed for color develop-  
 10 ment in accordance with the following process.

Processing Steps	Temperature	Time
Color Development	33 ° C	3 min 30 sec
Bleach-fixation	33 ° C	1 min 30 sec
Rinsing in water	33 ° C	3 min
Drying	50 to 80 ° C	2 min

The respective processing solutions had the following compositions:

Color Developer:	
Benzyl alcohol	12 ml
Diethylene glycol	5 ml
Potassium carbonate	25 g
Sodium chloride	0.1 g
Sodium bromide	0.5 g
Sodium sulfite anhydride	2 g
Hydroxylamine sulfate	2 g
Brightening agent	1 g
4-ethyl-N- $\beta$ -methanesulfonamido-ethyl-3-methyl-4-aminoaniline sulfate	4 g
Water to make	1 liter
NaOH to make	pH 10.2

Bleach-fixing Solution:	
Ammonium thiosulfate	124.5 g
Sodium metabisulfite	13.3 g
Sodium sulfite anhydride	2.7 g
Ammonium EDTA/iron (III)	65 g
Color developer	100 ml
pH was adjusted to 6.7 to 6.8 and water was added to make 1 liter.	

Using the above-mentioned processing solution, the color development was carried out in a conventional roller-transport type developing machine whereupon the replenishment of the replenishers was effected normally and the processing solutions used had almost equilibrated compositions.

Next, the magenta reflection density (stain) in the non-image part of each sample was measured after one hour from the development. Further, the magenta reflection density (stain) in the non-image part of each sample was also measured, after the samples were left at 80 ° C (70% RH) for 3 days or were left at room temperature for 50 days. The results are set forth in Table 8, where the increment of the stain from that measured in one hour after the color development is shown.

Table 8

Sample	Magenta Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Magenta Density 80°C/70% RH, Room Temp.,		Notes
				3 Days	50 Days	
G	M-23	-	-	0.18	0.15	Comparison
G-1	"	I - 1	30	0.05	0.02	Invention
G-2	"	I - 6	"	0.06	0.01	"
G-3	"	I - 13	"	0.05	0.02	"
G-4	M-13	-	-	0.08	0.06	Comparison
G-5	"	I - 2	30	0.05	0.02	Invention
G-6	"	I - 16	"	0.04	0.02	"
G-7	"	I - 22	"	0.04	0.02	"
G-8	M-23	I - 61	20	0.03	0.01	"
G-9	"	I - 67	"	0.02	0.01	"
G-10	"	I - 85	"	0.04	0.02	"
G-11	"	I - 87	"	0.04	0.01	"
G-12	"	I - 86	"	0.03	0.02	"

As is apparent from Table 8, the effect of preventing the generation of stains after storage by the compounds of the present invention is remarkable, and in particular, the compounds used in the invention are sufficiently effective even when the composition of the development processing solution used does not vary but is constant.

## EXAMPLE 10



# EP 0 258 662 B1

A color photographic material (Sample H) was prepared as follows:

The following first to eleventh layers were coated on a paper support both surfaces of which had been laminated with polyethylene to obtain the color photographic material. The polyethylene coated on the side of the first layer contained titanium white as a white pigment and a slight amount of ultramarine as a bluish dye.

The light-sensitive layers had the following compositions. All the amounts coated were designated by the unit of g/m<sup>2</sup>, whereas the amount of the silver halide coated was designated by the unit of g/m<sup>2</sup> as Ag.

First Layer (Anti-halation Layer):	
Black colloidal silver	0.01
Gelatin	0.2

Second Layer (Red-sensitive Layer of Low Sensitivity):	
Silver iodobromide emulsion (silver iodide: 3.5 mol%, mean grain size: 0.7 μ) spectral-sensitized with Red Sensitizer Dye (*5 and *4)	0.15 as Ag
Gelatin	1.0
Cyan coupler (*3)	0.30
Anti-fading agent (*2)	0.15
Coupler solvent (*15 and *1)	0.06

Third Layer (Red-sensitive Layer of High Sensitivity):	
Silver iodobromide emulsion (silver iodide: 8.0 mol%, mean grain size: 0.7 μ) spectral-sensitized with Red Sensitizer Dye (*5 and *4)	0.10 as Ag
Gelatin	0.50
Cyan coupler (*3)	0.10
Anti-fading agent (*2)	0.05
Coupler solvent (*15 and *1)	0.02

Fourth Layer (Interlayer):	
Yellow colloidal silver	0.02
Gelatin	1.00
Color mixing preventing agent (*14)	0.08
Color mixing preventing agent solvent (*13)	0.16
Polymer latex (*6)	0.40

Fifth Layer (Green-sensitive Layer of Low Sensitivity):	
Silver iodobromide emulsion (silver iodide: 2.5 mol%, mean grain size: 0.4 μ) spectral-sensitized with Green Sensitizer Dye (*12)	0.20 as Ag
Gelatin	0.70
Magenta coupler (*11)	0.40
Anti-fading agent A (*10)	0.05
Anti-fading agent B (*9)	0.05
Anti-fading agent C (*8)	0.02
Coupler solvent (*18)	0.60

## Sixth Layer (Green-sensitive Layer of High Sensitivity):

Silver iodobromide emulsion (silver iodide: 3.5 mol%, mean grain size: 0.9 $\mu$ ) spectral-sensitized with Green Sensitizer Dye (*12)	0.20 as Ag
Gelatin	0.70
Magenta coupler (*11)	0.40
Anti-fading agent A (*10)	0.05
Anti-fading agent B (*9)	0.05
Anti-fading agent C (*8)	0.02
Coupler solvent (*18)	0.60

## Seventh Layer (Yellow Filter Layer):

Yellow colloidal silver	0.20
Gelatin	1.00
Color mixing preventing agent (*14)	0.06
Color mixing preventing agent solvent (*13)	0.24

## Eighth Layer (blue-sensitive Layer of Low Sensitivity):

Silver iodobromide emulsion (silver iodide: 2.5 mol%, mean grain size: 0.5 $\mu$ ) spectral-sensitized with Blue Sensitizer Dye (*16)	0.15 as Ag
Gelatin	0.50
Yellow coupler (*15)	0.25
Coupler solvent (*18)	0.05

## Ninth Layer (Blue-sensitive Layer of High Sensitivity):

Silver iodobromide emulsion (silver iodide: 2.5 mol%, mean grain size: 1.4 $\mu$ ) spectral-sensitized with Blue Sensitizer Dye (*16)	0.20 as Ag
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## Tenth Layer (Ultraviolet Absorbing Layer):

Gelatin	1.50
Ultraviolet absorbent (*19)	1.0
Ultraviolet absorbent solvent (*18)	0.30
Color mixing preventing agent (*17)	0.08

## Eleventh Layer (Protective Layer):

Gelatin	1.0
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The compounds used in the above-mentioned layers are as follows:

- (\*1) Dioctyl phthalate
- (\*2) 2-(2-Hydroxy-3-sec-butyl-5-t-butylphenyl)benzotriazole
- (\*3) 2-[ $\alpha$ -(2,4-di-t-amyloxy)butanamido]-4,6-dichloro-5-ethylphenol]
- (\*4) 5,5'-Dichloro-3,3'-di(3-sulfobutyl)-9-ethylthia-carbocyanine/Na-salt
- (\*5) Triethylammonium 3-[2-{2-[3-(3-sulfopropyl)naphtho(1,2-d)thiazolin-2-ylidenemethyl]-1-butenyl}-3-naphtho(1,2-d)thiazolino]propanesulfonate
- (\*6) Polyethyl acrylate

- (<sup>\*</sup>7) Trioctyl phosphate  
 (<sup>\*</sup>8) 2,4-Di-t-hexylhydroquinone  
 (<sup>\*</sup>9) Di-(2-hydroxy-3-t-butyl-5-methylphenyl)methane  
 (<sup>\*</sup>10) 3,3,3',3'-Tetramethyl-5,6,5',6'-tetrapropoxy-1,1'-bisspiroindane  
 5 (<sup>\*</sup>11) 3-(2-Chloro-5-tetradecanamidonailino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one  
 (<sup>\*</sup>12) 5,5'-Diphenyl-9-ethyl-3,3'-disulfopropoxyloxycarbocyanine/Na-salt  
 (<sup>\*</sup>13) O-cresyl phosphate  
 (<sup>\*</sup>14) 2,4-Di-t-octylhydroquinone  
 10 (<sup>\*</sup>15)  $\alpha$ -Pivaloyl- $\alpha$ -[(2,4-dioxo-1-benzyl-5-ethoxyhydantoin-3-yl)-2-chloro-5-( $\alpha$ -2,4-dioxo-5-  
 amyphenoxy)butanamino]acetanilide  
 (<sup>\*</sup>16) Teithylammonium 3-[2-(3-benzylrhodanine-5-ylidene)-3-benzoxazoliny]propanesulfonate  
 (<sup>\*</sup>17) 2,4-Di-sec-octylhydroquinone  
 (<sup>\*</sup>18) Trinonyl phosphate  
 15 (<sup>\*</sup>19) 5-Chloro-2-(2-hydroxy-3-t-butyl-5-t-octyl)phenylbenzotriazole

In the same manner as the preparation of Sample (H), except that the combination of the Magneta Coupler and the compound used in the invention as shown in the following Table 9 was used in the fifth and sixth layers in place of the Magenta Coupler of Sample (H), Sample (H-1) through (H-6) were also prepared.

These samples thus prepared were exposed to light through an optical wedge and then processed for color development in accordance with the following procedure.

Processing Steps	Temperature	Time
First Development (Black-and-white development)	38° C	1 min 15 sec
Rinsing in Water	38° C	1 min 30 sec
25 Reversal Exposure	100 lux or more	1 min or more
Color Development	38° C	2 min 15 sec
Rinsing in Water	38° C	45 sec
Bleach-fixation	38° C	2 min 00 sec
30 Rinsing in Water	38° C	2 min 15 sec

The processing solutions used had the following compositions.

First Developer:	
Penta-sodium nitrilo-N,N,N-trimethylene-phosphonate	0.6 g
Penta-sodium diethylenetriamine-pentaacetate	4.0 g
Potassium sulfite	30.0 g
Potassium thiocyanate	1.2 g
Potassium carbonate	35.0 g
40 Potassium hydroquinone-monosulfonate	25.0 g
Diethylene glycol	15.0 ml
1-Phenyl-4-hydroxypethyl-4-methyl-3-pyrazolidone	2.0 g
Potassium bromide	0.5 g
Potassium iodide	5.0 mg
45 Water to make	1 liter
	(pH 9.70)

# EP 0 258 662 B1

Color Developer:	
Benzyl alcohol	15.0 ml
Diethylene glycol	12.0 ml
3,6-Dithio-1,8-octanediol	0.2 g
Penta-sodium nitrilo-N,N,N-trimethylene phosphonate	0.5 g
Penta-sodium diethylenetriamine-penta acetate	2.0 g
Sodium sulfite	2.0 g
Potassium carbonate	25.0 g
Hydroxylamine sulfate	3.0 g
N-Ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
Potassium bromide	0.5 g
Potassium iodide	1.0 mg
Water to make	1 liter
	(pH 10.40)

Bleach-fixing Solution:	
2-Mercapto-1,3,4-triazole	1.0 g
Disodium ethylenediamine-tetraacetate/di-hydrate	5.0 g
Ammonium ethylenediamine-tetraacetate/Fe(III)/mono-hydrate	80.0 g
Sodium sulfite	15.0 g
Sodium thiosulfate (700 g/liter-solution)	160.0 ml
Glacial acetic acid	5.0 ml
Water to make	1 liter
	(pH 6.50)

Next, the magenta reflection density (stain) in the non-image part of each sample was measured after the development. Further, the magenta reflection density (stain) in the non-image part of each sample was also measured, after the samples were left at 80 °C (70% RH) for 3 days or were left at room temperature for 80 days. The results are set forth in Table 9, where in increment of the stain from that measured at one hour after the color development is shown.

Table 9

Sample	Magenta Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Magenta Density		Notes
				80°C/70% RH, 3 Days	Room Temp., 80 Days	
H	M-13	-	-	0.06	0.04	Comparison
H-1	"	I - 2	30	0.03	0.02	Invention
H-2	"	I - 7	"	0.02	0.01	"
H-3	"	I - 24	"	0.03	0.02	"
H-4	M-23	-	-	0.14	0.12	Comparison
H-5	"	I - 1	30	0.03	0.01	Invention
H-6	"	I - 6	"	0.04	0.01	"

As is apparent from Table 9, the effect of preventing the generation of stains after storage by the compounds used in the present invention is remarkable, and the effect does not vary but is constant even when the constitution of the photographic materials to be processed and the process for the development vary.

#### EXAMPLE 11

A color photographic material was prepared by multiple-coating the first to the fourteenth layers (see below) on a paper support laminated with polyethylene on both sides. The polyethylene on the side to be coated with the first layer contained titanium white as a white pigment and a slight amount of ultramarine as a bluish dye.

#### Composition of light-sensitive layers

The compositions of the light-sensitive layers employed are indicated below in terms of components and the amounts coated, the latter being designated by the unit of g/m<sup>2</sup>. The amount of silver halide coated is designated in terms of silver deposit. All of the emulsions except the one incorporated in the 14th layer were prepared by the following method.

#### Preparation of emulsions

Aqueous solutions of potassium bromide and silver nitrate were added simultaneously under vigorous agitation at 75 °C over a period of about 20 minutes to an aqueous solution of gelatin containing 0.3 g of 3,4-dimethyl-1,3-thiazoline-2-thione per mole of Ag. As a result, a monodispersed silver bromide emulsion comprising octahedral grains with mean size of 0.40 µm was obtained. The emulsion was chemically sensitized by heating at 75 °C for 80 minutes in the presence of 6 mg of sodium thiosulfate and 7 mg of chloroauric acid (tetrahydrate) per mole of Ag. Further crystal growth was conducted in the same precipitation environment as employed above, with the previously prepared AgBr grains used as core grains. As a result of this crystal growth, a monodispersed core/shell type AgBr emulsion comprising octahedral grains with an average size of 0.7 µm was finally obtained. The coefficient of variation in grain size was 10%.

The emulsion was chemically sensitized by heating at 60 °C for 60 minutes in the presence of 1.5 mg of sodium thiosulfate and 1.5 mg of chloroauric acid (tetrahydrate) per mole of Ag, so as to prepare a silver halide emulsion for internal latent image type.

First Layer (Anti-halation Layer):	
Black colloidal silver	0.10
Gelatin	1.30

Second Layer (Interlaye):	
Gelatin	0.70

Third Layer (Red-sensitive Layer of Low Sensitivity):	
Silver bromide emulsion (mean grain size: 0.3 µm; size distribution, 8%; octahedral grain) spectrally sensitized with Red Sensitizer Dyes (ExS-1, 2 and 3)	0.06
Silver bromide emulsion (mean grain size: 0.45 µm; size distribution, 10%; octahedral grain) spectrally sensitized with Red Sensitizer Dyes (ExS-1, 2 and 3)	0.10
Gelatin	1.00
Cyan coupler (ExC-1)	0.14
Cyan coupler (ExC-2)	0.07
Anti-fading agent (Cpd-2, 3, 4 and 9 in equal amounts)	0.12
Coupler dispersant (Cpd-5)	0.3
Coupler solvent (Solv-1, 2 and 3 in equal amounts)	0.06

**Fourth Layer (Red-sensitive Layer of High Sensitivity):**

Silver bromide emulsion (mean grain size: 0.75 $\mu\text{m}$ ; size distribution, 10%; octahedral grain) spectrally sensitized with Red Sensitizer Dyes (ExS-1, 2 and 3)	0.15
Gelatin	1.00
Cyan coupler (ExC-1)	0.20
Cyan coupler (ExC-2)	0.10
Anti-fading agent (Cpd-2, 3, 4 and 9 in equal amounts)	0.15
Coupler dispersant (Cpd-5)	0.03
Coupler solvent (Solv-1, 2, and 3 in equal amounts)	0.10

**Fifth Layer (Interlayer):**

Gelatin	1.00
Color mixing preventing agent (Cpd-7)	0.08
Color mixing preventing agent solvent (Solv-4 and 5)	0.16
Polymer Latex (Cpd-8)	0.10

**Sixth Layer (Green-sensitive Layer of Low Sensitivity):**

Silver bromide emulsion (mean grain size: 0.28 $\mu\text{m}$ ; size distribution, 10%; octahedral grain) spectrally sensitized with Green Sensitizer Dyes (ExS-3 and 4)	0.04
Silver bromide emulsion (mean grain size: 0.45 $\mu\text{m}$ ; size distribution, 8%; octahedral grain) spectrally sensitized with Green Sensitizer Dyes (ExS-3 and 4)	0.06
Gelatin	0.80
Magenta coupler (ExM-1)	0.10
Anti-fading agent (Cpd-9)	0.10
Anti-stain agent (Cpd-10)	0.01
Anti-stain agent (Cpd-11)	0.001
Coupler dispersant (Cpd-5)	0.05
Coupler solvent (Solv-4 and 6 in equal amounts)	0.15

**Seventh Layer (Green-sensitive Layer of High Sensitivity):**

Silver bromide emulsion (mean grain size: 0.9 $\mu\text{m}$ ; size distribution, 10%; octahedral grain) spectrally sensitized with Green Sensitizer Dyes (ExS-3)	0.10
Gelatin	0.80
Magenta coupler (ExM-1)	0.10
Anti-fading agent (Cpd-9)	0.10
Anti-stain agent (Cpd-10)	0.01
Anti-stain agent (Cpd-11)	0.001
Coupler dispersant (Cpd-5)	0.05
Coupler solvent (Solv-4 and 6 in equal amounts)	0.15

**Eighth Layer (Interlayer)**

Same as the fifth layer.

## Ninth Layer (Yellow Filter Layer):

Yellow colloidal silver	0.20
Gelatin	1.00
Color mixing preventing agent (Cpd-7)	0.06
Color mixing preventing agent solvent (Solv-4 and 5 in equal amount)	0.15
Polymer Latex (Cpd-8)	0.10

## Tenth Layer:

Same as the fifth layer.

## Eleventh Layer (Blue-sensitive Layer of Low Sensitivity):

Silver bromide emulsion (mean grain size: 0.35 $\mu$ m; size distribution, 8%; tetradecahedral grain) spectrally sensitized with Blue Sensitizer Dyes (ExS-5)	0.07
Silver bromide emulsion (mean grain size: 0.45 $\mu$ m; size distribution, 10%; tetradecahedral grain) spectrally sensitized with Blue Sensitizer Dyes (ExS-5)	0.10
Gelatin	0.50
Yellow coupler (ExY-1)	0.20
Anti-stain agent (Cpd-11)	0.001
Anti-fading agent (Cpd-6)	0.10
Coupler dispersant (Cpd-5)	0.05
Coupler solvent (Solv-2)	0.05

## Twelfth Layer (Blue-sensitive Layer of High Sensitivity):

Silver bromide emulsion (mean grain size: 1.2 $\mu$ m; size distribution, 10%; tetradecahedral grain) spectrally sensitized with Blue Sensitizer Dyes (ExS-5 and 6)	0.25
Gelatin	1.00
Yellow coupler (ExY-1)	0.40
Anti-stain agent (Cpd-11)	0.002
Anti-fading agent (Cpd-6)	0.10
Coupler dispersant (Cpd-5)	0.05
Coupler solvent (Solv-2)	0.10

## Thirteenth Layer (Ultraviolet Absorbing Layer):

Gelatin	1.50
Ultraviolet absorbent (Cpd-1, 3 and 13 in equal amounts)	0.06
Color mixing preventing agent (Cpd-6 and 14 in equal amounts)	0.06
Dispersant (Cpd-5)	0.08
Ultraviolet absorbent solvent (Solv-1 and 2 in equal amounts)	0.15
Anti-irradiation dye (Cpd-15 and 16 in equal amounts)	0.02
Anti-irradiation dye (Cpd-17 and 18 in equal amounts)	0.02



Fourteenth Layer (Protective Layer):	
Fine silver chlorobromide grains (AgCl, 97 mol%; mean size, 0.2 $\mu$ m)	0.15
Modified POVAL	0.02
Gelatin	1.50
Gelatin hardener (H-1)	0.17

Each of the light-sensitive layers contained  $10^{-3}$  wt% of N-I-9 (as a nucleating agent) and  $10^{-2}$  wt% of ExZS-1 (as a nucleation accelerator) on the basis of the silver halide deposit in each layer.

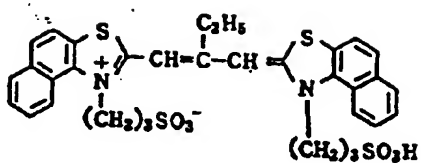
Each of the 1st to 14th layers contained Alkanol XC (product of Dupont) and a sodium alkylbenzenesulfonate as emulsification and dispersion aids, and a succinic acid ester and Magefac F-120 (product of Dainippon Ink & Chemicals, Inc.) as coating aids. Stabilizers (Cpd-19, 20 and 21) were incorporated in the silver halide or colloidal silver containing layers. The sample prepared using the above-mentioned layers was designated (I). The compounds employed in this example are identified below.

Additional samples were prepared by the same procedures as employed for the preparation of sample (I), except that the magenta couplers and Cpd-10 in the 6th and 7th layers were changed to those indicated in Table 10.

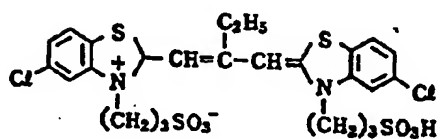
The samples thus prepared were exposed to light through an optical wedge, then processed for color development in accordance with Processing Scheme C.

In the next place, the magenta reflection density (stain) in the non-image area of each sample was measured after the development. Further, the magenta reflection density (stain) in the non-image area of each sample was also measured, after the samples were left at 80 °C (70% RH) for 3 days or were left at room temperature and 80 days. The results are set forth in Table 11, where the increment of the stain from that measured at one hour after the color development is shown.

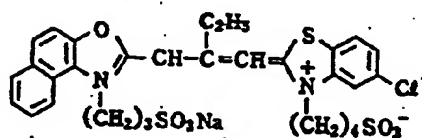
(ExS-1)



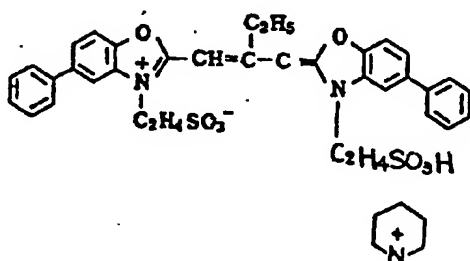
(ExS-2)



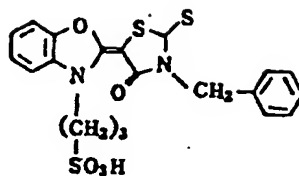
(ExS-3)



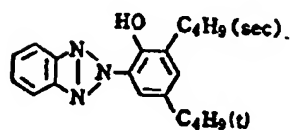
(ExS-4)



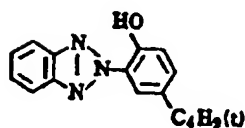
(Ex 5-5)



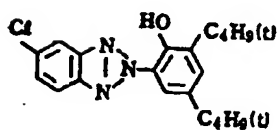
(Cpd-1)



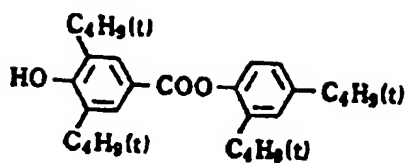
(Cpd-2)



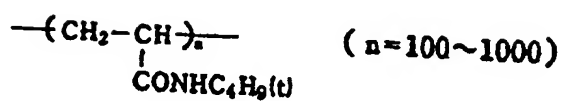
(Cpd-3)



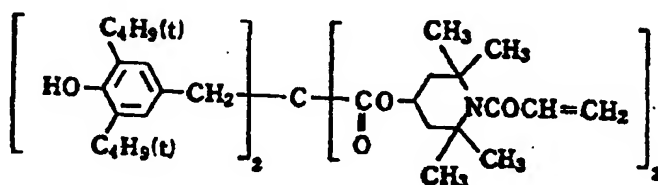
(Cpd-4)



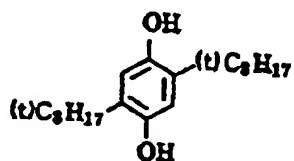
(Cpd-5)



(Cpd-6)



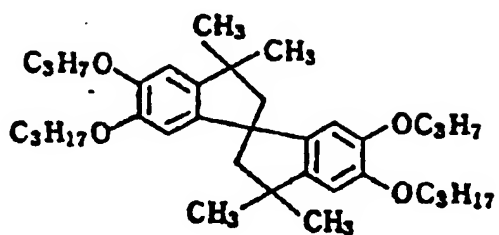
(Cpd-7)



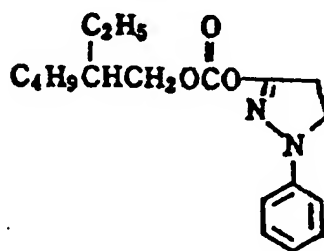
(Cpd-8)

Polyethyl acrylate

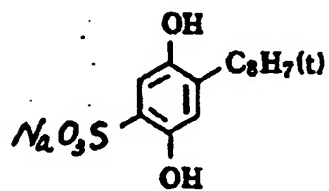
(Cpd-9)



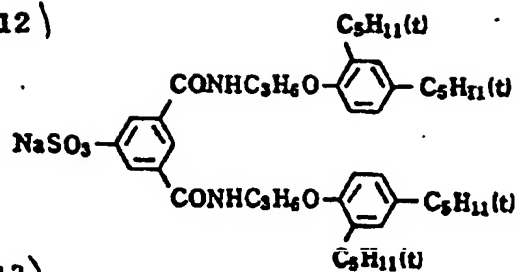
(Cpd-10)



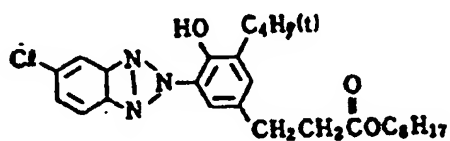
(Cpd-11)



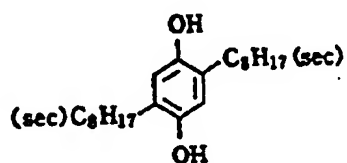
(Cpd-12)



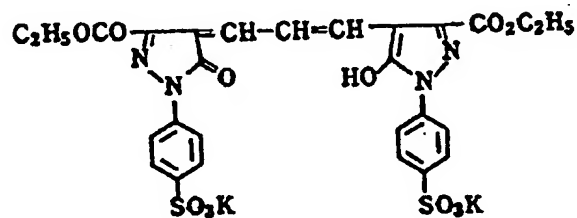
(Cpd-13)



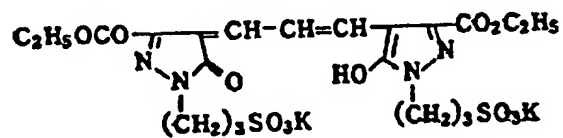
(Cpd-14)



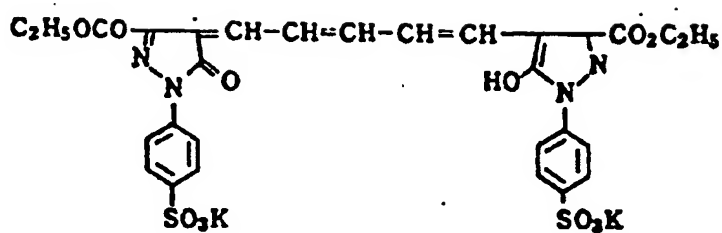
(Cpd-15)



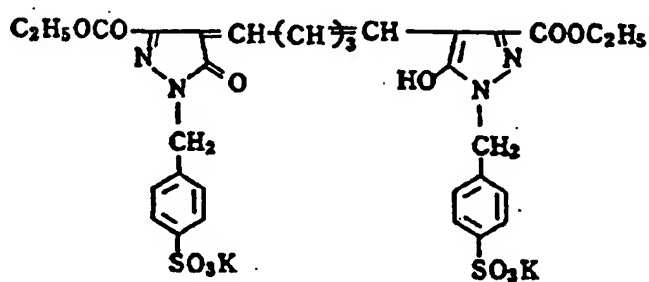
(Cpd-16)



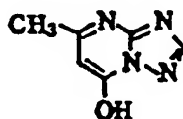
(Cpd-17)



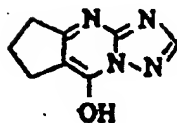
(Cpd-18)



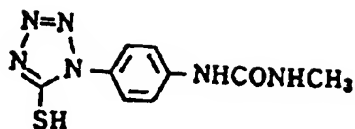
(Cpd-19)



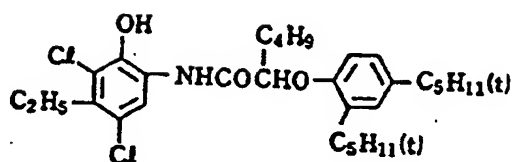
(Cpd-20)



(Cpd-21)



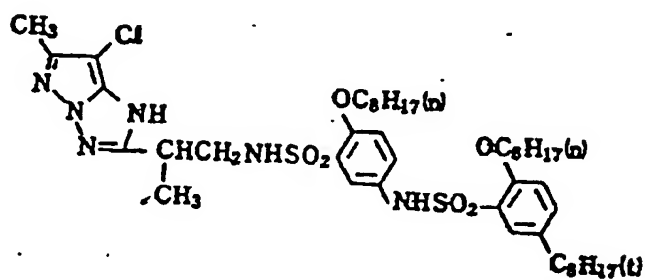
(EXC-1)



(EXC-2)



(EXM-1)





5



- 25**

## 30



## 45



# EP 0 258 662 B1

Steps	Time (sec)	Temperature (°C)
Color development	70	38
Bleach-fixing	45	38
Rinsing in water (1)	45	38
Rinsing in water (2)	45	38

Rinsing water was replenished by the "countercurrent replenishing system" in which the rinse bath (2) was replenished, with the overflow from the rinse bath (2) being introduced into the rinse bath (1).

Color Developer:	
	Mother Liquid
Diethylenetriaminepentaacetic acid	0.5 g
1-Hydroxyethylidene-1,1-diphosphonic acid	0.5 g
Diethylene glycol	8.0 g
Benzyl alcohol	12.0 g
Sodium bromide	0.7 g
Sodium sulfite	2.0 g
N,N-diethylhydroxylamine	3.5 g
Triethylenediamine(1,4-diazabicyclo-[2,2,2]octane)	3.5 g
3-Methyl-4-amino-N-ethyl-N-(β-methane-sulfonamidoethyl)aniline	6.0 g
Potassium carbonate	30.0 g
Brightener (stilbene based compound)	1.0 g
Pure water	to make 1000 ml
pH	10.50

pH adjustment was achieved by addition of potassium hydroxide or hydrochloric acid.

Bleach-fixing Solution:	
	Mother Liquid
Ammonium thiosulfate	110 g
Sodium hydrogen sulfite	14.0 g
Ammonium ethylenediaminetetraacetate/ Fe(III)/dihydrate	40.0 g
Ethylenediaminetetraacetic acid	
Disodium salt (dihydrate)	4.0 g
Pure water	to make 1000 ml
pH	7.0

pH adjustment was achieved by addition of aqueous ammonia or hydrochloric acid.

## Rinsing Water:

Pure water was used.

Pure water was obtained from tap water that had been subjected to an ion-exchange treatment so that all cations other than hydrogen ions and all anions except hydroxyl ions were reduced to concentration of no more than 1 ppm.

Table 10

Sample	Magenta Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Magenta Density		Notes
				80°C/70% RH, 3 Days	Room Temp., 80 Days	
I	ExM-1 (M-23)	Cpd - 10	10	0.05	0.05	Comparison
I-1	"	-	-	0.11	0.10	"
I-2	"	I - 61	10	0.01	0.01	Invention
I-3	"	I - 67	"	0.01	0.01	"
I-4	"	I - 85	"	0.02	0.01	"
I-5	"	I - 87	"	0.02	0.02	"
I-6	"	I - 110	"	0.01	0.01	"
I-7	M-27	-	-	0.06	0.05	Comparison
I-8	"	I - 28	10	0.02	0.01	Invention
I-9	"	I - 35	"	0.01	0.02	"
I-10	"	I - 46	"	0.01	0.01	"
I-11	"	I - 50	"	0.02	0.01	"
I-12	"	I - 53	"	0.01	0.02	"
I-13	"	I - 59	"	0.01	0.01	"
I-14	"	I - 86	"	0.01	0.01	"

Substantially the same results as shown in Table 10 were attained even when the emulsions were changed from silver bromide emulsions to silver chlorobromide emulsions having varying concentrations of silver chloride (0.5 to 99.5 mol%).

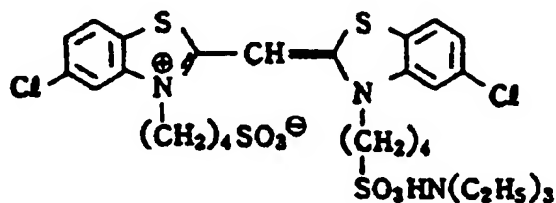
The samples were subjected to a color-fading test with a xenon lamp under the same condition as employed in Example 2. All samples exhibited high resistance to color fading by light except that sample I

was inferior to samples I-1 and I-7. As is clear from these results and from the data shown in Table 11, the compounds used in the present invention are highly effective in preventing the occurrence of stains in magenta image during storage. In addition, the compounds have a noticeable capability of improving resistance to color fading by light.

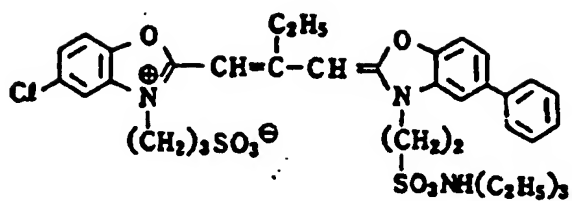
5 The compounds used in Examples 12 to 14 are shown below.

### Sensitizing Dyes:

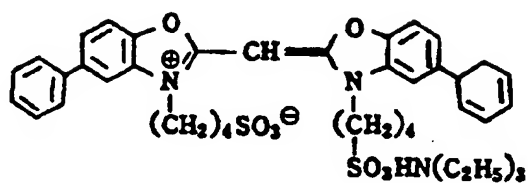
#### ExS-1



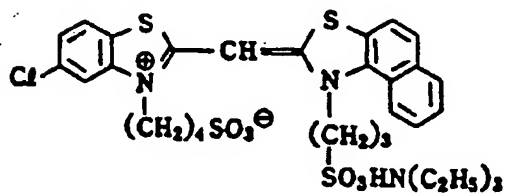
## ExS-2



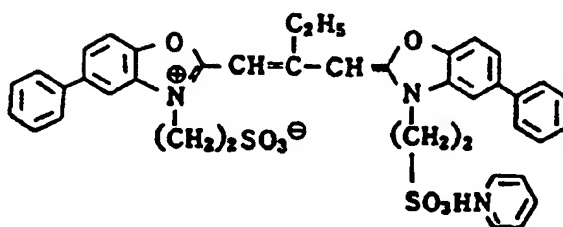
## ExS-3



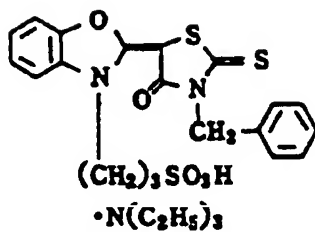
## ExS-4



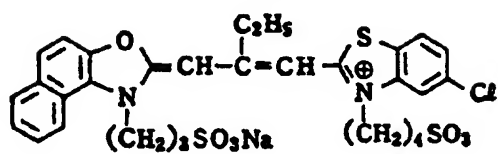
## ExS-5



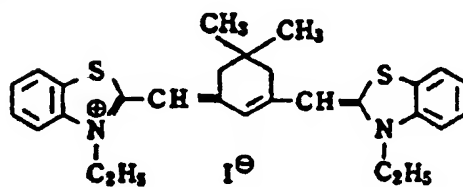
ExS-6



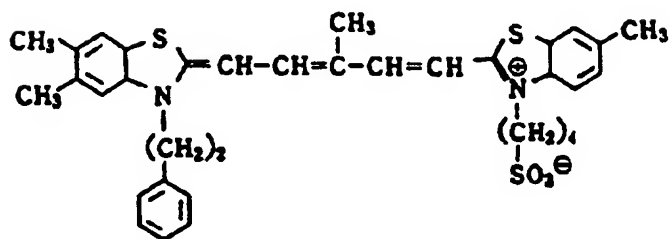
ExS-7



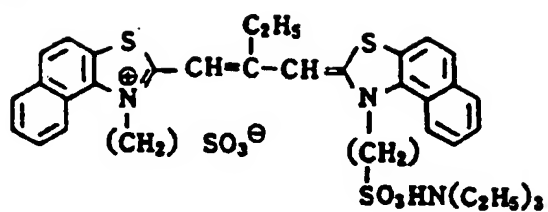
ExS-8



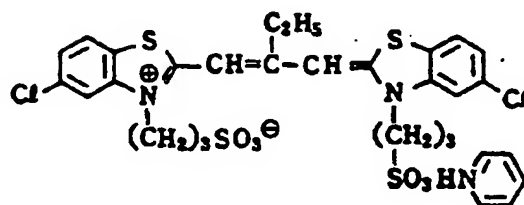
ExS-9



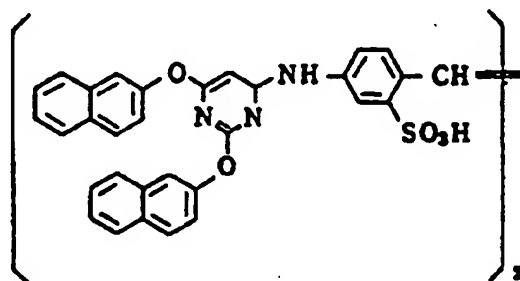
ExS-10



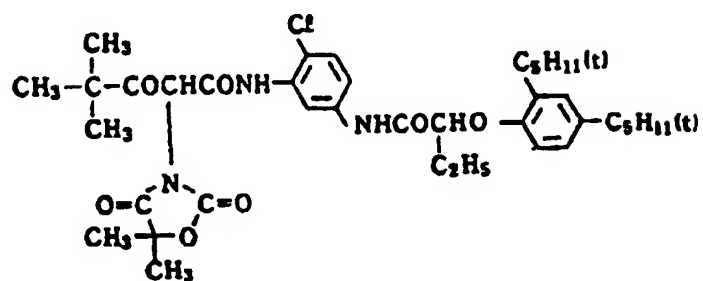
ExS-11



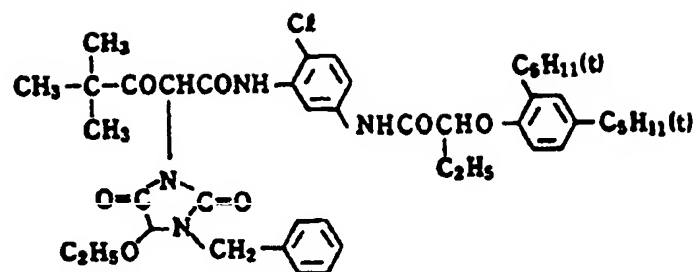
ExS-12



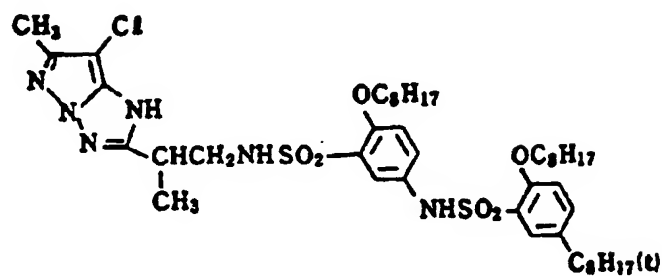
ExY-1



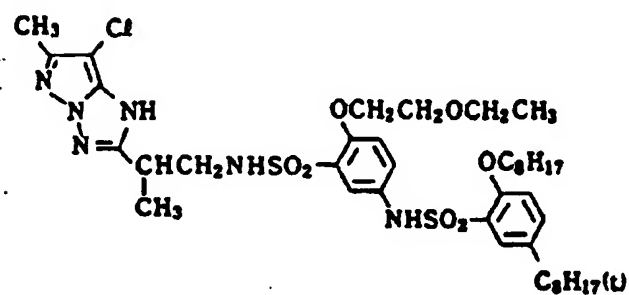
## ExY-2



## ExM-1

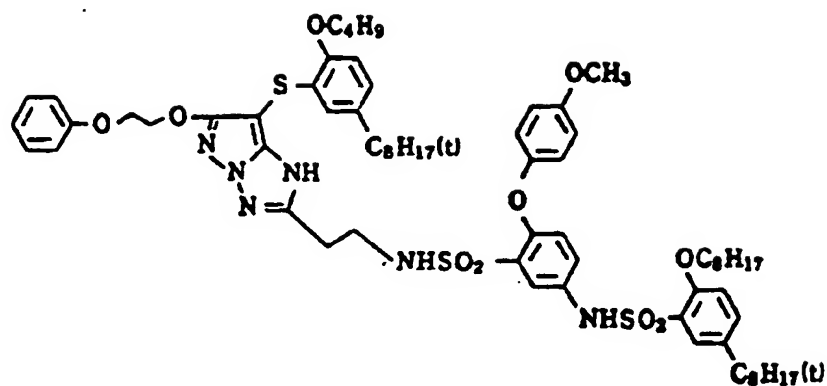


## ExM-2

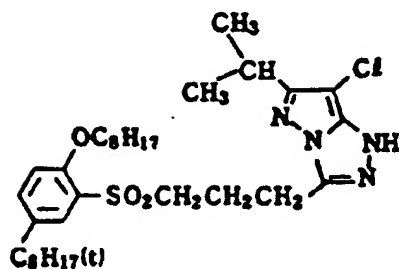




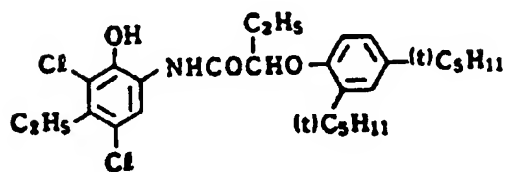
## ExM-3



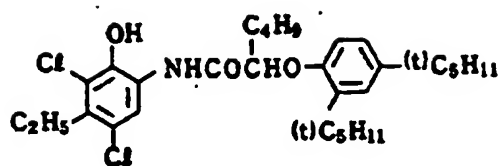
## ExM-4



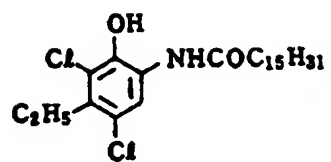
## ExC-1



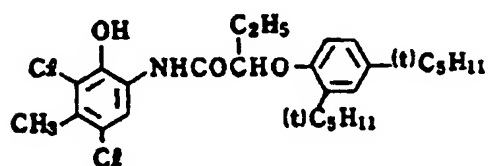
## ExC-2



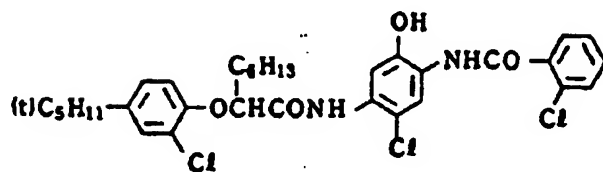
## ExC-3



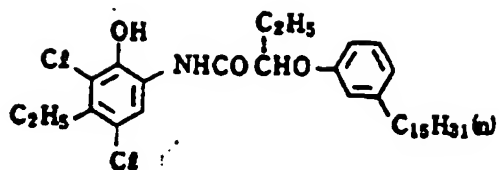
## ExC-4



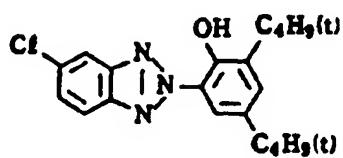
## ExC-5



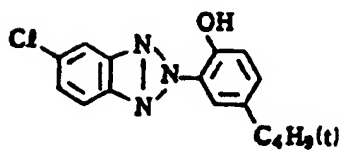
ExC-6



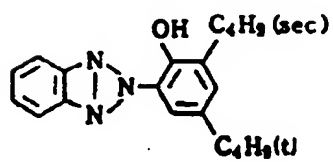
Cpd-1



Cpd-2



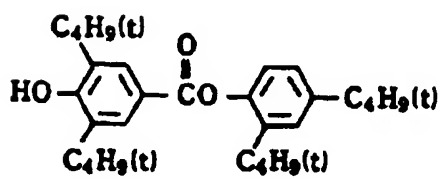
Cpd-3



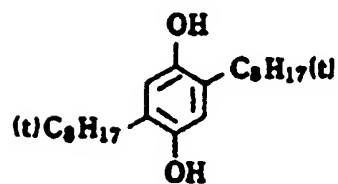
Cpd - 4



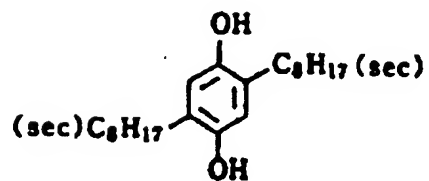
Cpd - 5



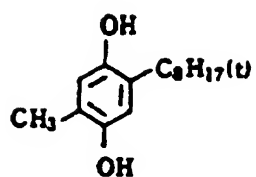
Cpd - 6



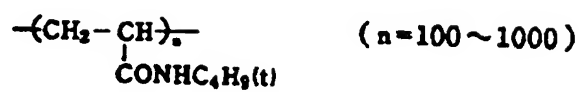
Cpd - 7



Cpd-8



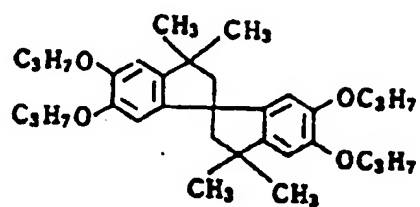
Cpd-9



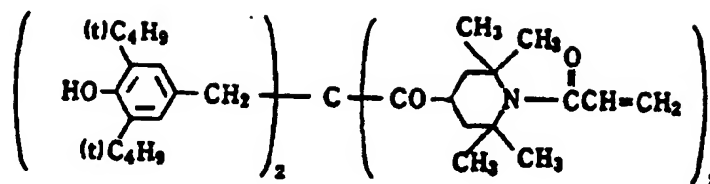
Cpd-10

Polyethyl Acrylate Latex

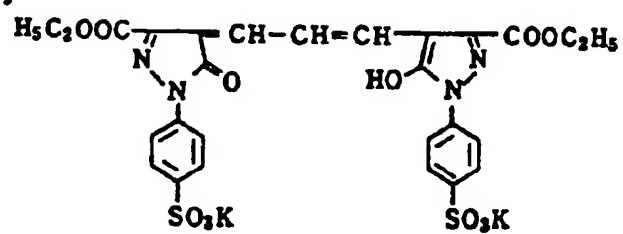
Cpd-11



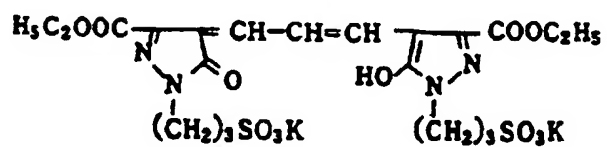
Cpd - 12



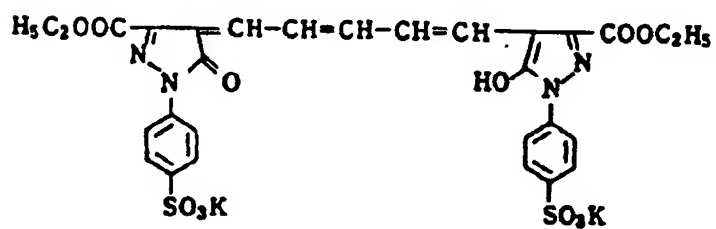
Cpd - 13



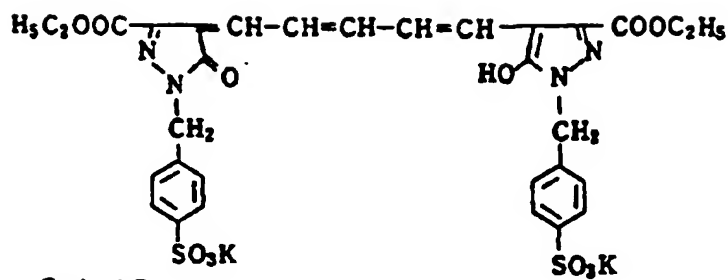
Cpd - 14



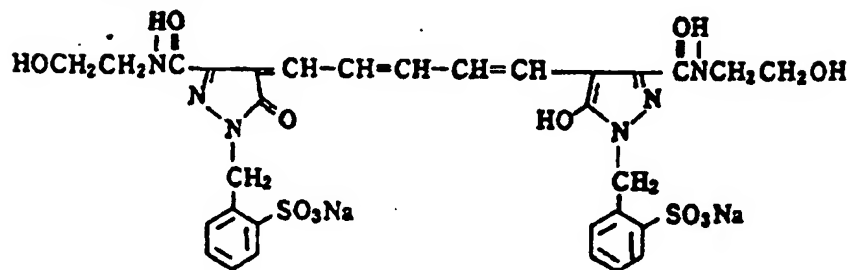
Cpd - 15



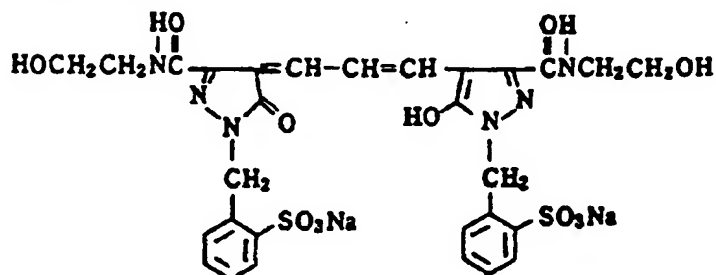
Cpd - 16



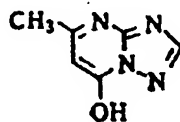
Cpd - 17



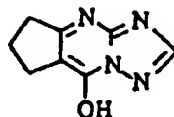
Cpd - 18



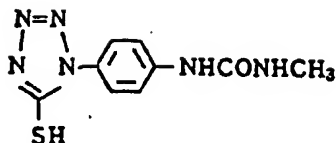
Cpd - 19



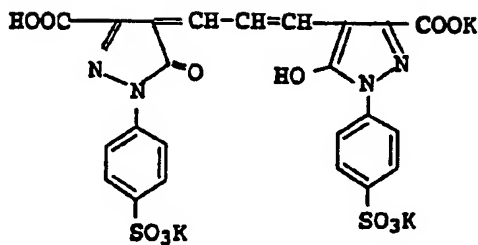
(Cpd-20)



(Cpd-21)



(Cpd-22)



- |        |                            |
|--------|----------------------------|
| Solv-1 | Di(2-ethylhexyl)phthalate  |
| Solv-2 | Trinonyl phosphate         |
| Solv-3 | Di(3-methylhexyl)phthalate |
| Solv-4 | Tricresyl phosphate        |
| Solv-5 | Dibutyl phthalate          |
| Solv-6 | Trioctyl phosphate         |

**EXAMPLE 12**

A multi-layered color photographic paper J was prepared by coating a plurality of layers as shown below on a paper support laminated with polyethylene on both sides. The necessary coating solutions were prepared in the following manner.

**Preparation of First Layer Coating Solution:**

10.2 g of yellow coupler ExY-1), 9.1 g of yellow coupler (ExY-2) and 4.4 g of a color image stabilizer (Cpd-12) were dissolved in 27.2 cc of ethyl acetate and 7.7 cc (8.0 g) of a high-boiling point solvent (Solv-5) and the resulting solution was emulsified and dispersed in 185 cc of a 10% aqueous gelatin solution containing 8 cc of 10% sodium dodecylbenzenesulfonate. The resulting emulsified dispersion was mixed with emulsins EM-1 and EM-2 (see below) and a solution was made. The concentration of gelatin in the solution was so adjusted as to provide the composition indicated below. The so prepared solution was used



as a coating solution for the first layer. Coating solutions for the second to seventh layers were prepared in a similar manner. A sodium salt of 1-oxy-3,5-dichloro-s-triazine was used as a gelatin hardener in each of the layers.

#### 5 Layer Composition:

The compositions of the individual layers are shown below, in which the numerals denote the amounts of individual components added (g/m<sup>2</sup>) except that the amounts of silver halide emulsions are expressed in terms of silver deposit.

10

#### Support:

Polyethylene Laminated Paper

(containing a white pigment (TiO<sub>2</sub>) and a bluish dye in the polyethylene on the side to be coated with the  
15 first layer)

20

25

First Layer (Blue-sensitive Layer):	
Monodispersed silver chlorobromide emulsion (EM-1) spectrally sensitized with Sensitizer Dye (ExS-1)	0.13
Monodispersed silver chlorobromide emulsion (EM-2) spectrally sensitized with Sensitizer dye (ExS-1)	0.13
Gelatin	1.86
Yellow coupler (ExY-1)	0.44
Yellow coupler (ExY-2)	0.39
Color image stabilizer (Cpd-12)	0.19
Solvent (Solv-5)	0.35

30

Second Layer (Color Mixing Preventing Layer):	
Gelatin	0.99
Color mixing preventing agent (Cpd-7)	0.08

35

40

45

Third Layer (Green-sensitive Layer):	
Monodispersed silver chlorobromide emulsion (EM-3) spectrally sensitized with Sensitizer Dye (ExS-2 and 3)	0.05
Monodispersed silver chlorobromide emulsion (EM-4) spectrally sensitized with Sensitizer Dye (ExS-2 and 3)	0.11
Gelatin	1.80
Magenta coupler (ExM-1)	0.38
Color image stabilizer (Cpd-11)	0.20
Solvent (Solv-4)	0.12
Solvent (Solv-6)	0.25

50

55

Fourth Layer (Ultraviolet Absorbing Layer):	
Gelatin	1.60
Ultraviolet absorber (Cpd-1/Cpd-2/Cpd-3 = 3/2/6 by weight ratio)	0.70
Color mixing preventing agent (Cpd-6)	0.05
Solvent (Solv-2)	0.27

Fifth Layer (Red-sensitive Layer):	
Monodispersed silver chlorobromide emulsion (EM-5) spectrally sensitized with Sensitizer Dye (ExS 8 and 12)	0.07
Monodispersed silver chlorobromide emulsion (EM-6) spectrally sensitized with Sensitizer Dye (ExS-8 and 12)	0.16
Gelatin	0.92
Cyan coupler (ExC-6)	0.32
Color image stabilizer (Cpd-2/Cpd-3/Cpd-4 = 3/4/2 by weight ratio)	0.17
Dispersant polymer (Cpd-9)	0.28
Solvent (Solv-4)	0.20

Sixth Layer (Ultraviolet Absorbing Layer):	
Gelatin	0.54
Ultraviolet absorber (Cpd-1/Cpd-3/Cpd-4 = 1/5/3 by weight ratio)	0.21
Solvent (Solv-4)	0.08

Seventh Layer (Protective Layer):	
Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (17% modification)	0.17
Liquid Paraffin	0.03

The sample prepared in this example contained CPd-15 and Cpd-22 as anti-irradiation dyes.

Each of the 1st to 7th layers contains Alkanol XC (product of Dupont) and a sodium alkylbenzenesulfonate as emulsification and dispersion aids, and a succinic acid ester and Magefax F-120 (product of Dainippon Ink & Chemicals, Inc.) as coating aids. Silver halides were stabilized by incorporation of Cpd-19 and 21. The silver halide emulsions employed in this example are characterized below.

Emulsion	Grain Morphology	Grain Size ( $\mu\text{m}$ )	Br Content (mol%)	Coefficient of Variation
EM-1	cubic	1.0	80	0.08
EM-2	cubic	0.75	80	0.07
EM-3	cubic	0.5	83	0.09
EM-4	cubic	0.4	83	0.10
EM-5	cubic	0.5	73	0.09
EM-6	cubic	0.4	73	0.10

Additional samples were prepared in the same manner as described above except that the magenta coupler in the third layer (green-sensitive layer) of Sample J was replaced by equimolar amounts of the magenta couplers shown in Table 11 which were combined with selected storability-improving compounds of the present invention as indicated in Table 11.

The samples thus prepared were exposed to light through an optical wedge, then processed by the following process (I) to form color images.

Process (I):

The samples exposed were subjected to running development with a Fuji Color Paper Processor FPRP 115 (Fuji Photo Film Co., Ltd.) under the conditions described below.

Step	Temperature (° C)	Time	Amount of Replenisher*	Tank Capacity (liter)
Color development	37	3 min 30 sec	200 ml	60
Bleach-fixing	33	1 min 30 sec	55 ml	40
Rinsing in water (1)	24 - 34	1 min	-	20
Rinsing in water (2)	24 - 34	1 min	-	20
Rinsing in water (3)	24 - 34	1 min	10 ml	20
Drying	70 - 80	1 min		

\* Per square meter of the light-sensitive material.

[The three rinsing tanks were connected in cascade in such a way that the overflowing rinsing replenisher ran in order from tank (3) to tank (1).]

Color Developer:		
	Tank Solution	Replenisher
Water	800 ml	800 ml
Diethylenetriaminepentaacetic acid	1.0 g	1.0 g
Nitrilotriacetic acid	2.0 g	2.0 g
Benzyl alcohol	15 ml	23 ml
Diethylene glycol	10 ml	10 ml
Sodium sulfite	2.0 g	3.0 g
Potassium bromide	1.2 g	-
Potassium carbonate	30 g	25 g
N-Ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	9.0 g
Hydroxylamine sulfate	3.0 g	4.5 g
Brightening agent (WHITEX 4B of Sumitomo Chemical Co., Ltd.)	1.0 g	2.0 g
Water to make	1000 ml	1000 ml
pH (at 25° C)	10.20	10.80

Bleaching-fixation Solution:		
	Tank Solution	Replenisher
Water	400 ml	400 ml
Ammonium thiosulfate (70 wt%)	150 ml	300 ml
Sodium sulfite	13 g	26 g
Ammonium ethylenediamine-tetraacetic acid iron (III)	55 g	110 g
Ethylenediaminetetraacetic acid disodium salt	5 g	10 g
Water to make	1000 ml	1000 ml
pH (at 25° C)	6.70	6.30

In the next place, the magenta reflection density (stain) in the non-image area of each of the light-sensitive materials was measured after the development. Further, the magenta reflection density (stain) in the non-image area of each sample was also measured, after the samples were left at 80° C (70% RH) for 3 days or were left at room temperature for 50 days. The results are, set forth in Table 11, where the increment of the stain from that measured at one hour after the color development is shown.

As will be clear from Table 11, the compounds used in the present invention are highly effective against magenta staining.

Table 11

Sample	Magenta Coupler	Additive	Amount Added (mol% to Coupler)	Increment of Magenta Density 80°C/70% RH, Room Temp.,		Notes
				3 Days	50 Days	
J	ExM-1	-	-	0.09	0.07	Comparison
J-1	"	I - 28	30	0.02	0.01	Invention
J-2	"	I - 35	"	0.02	0.01	"
J-3	"	I - 46	"	0.01	0.02	"
J-4	"	I - 50	"	0.01	0.01	"
J-5	ExM-2	-	-	0.09	0.06	Comparison
J-6	"	I - 61	20	0.01	0.01	Invention
J-7	"	I - 67	"	0.01	0.01	"
J-8	"	I - 85	"	0.02	0.01	"
J-9	"	I - 87	"	0.02	0.02	"
J-10	"	I - 110	"	0.01	0.01	"
J-11	ExM-3	-	-	0.06	0.03	Comparison
J-12	"	I - 53	30	0.01	0.01	Invention
J-13	"	I - 59	10	0.02	0.01	"
J-14	"	I - 86	"	0.01	0.01	"
J-15	ExM-4	-	-	0.08	0.07	Comparison
J-16	"	I - 61	20	0.01	0.01	Invention
J-17	"	I - 67	"	0.01	0.01	"
J-18	"	I - 110	"	0.02	0.01	"

## EXAMPLE 13

A sample prepared as in Example 12 was exposed to light through an optical wedge and subsequently processed by one of the following processes (II) to (V). Evaluation of resistance to magenta staining that

was conducted as in Example 12 showed that the comparative samples experienced increased magenta staining whereas the samples incorporating the compounds used in the present invention were substantially free from detectable stain.

5 Process (II):

Step	Temperature (° C)	Time
Color development	38	1 min and 40 sec
Bleach-fixing	30 - 34	1 min and 00 sec
Rinsing in water (1)	30 - 34	20 sec
Rinsing in water (2)	30 - 34	20 sec
Rinsing in water (3)	30 - 34	20 sec
Drying	70 - 80	50 sec
[The three rinsing tanks were connected in cascade in such a way that the overflowing rinsing solution ran in order from tank (3) to tank (1).]		

Color Developer:	
Water	800 ml
Diethylenetriaminepentaacetic acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid (60 wt%)	2.0 g
Nitrilotriacetic acid	2.0 g
1,3-Diamino-2-propanol	4.0 g
1,4-Diazabicyclo[2,2,2]octane	6.0 g
Potassium bromide	0.5 g
Potassium carbonate	30 g
N-Ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.5 g
N,N-diethylhydroxylamine sulfate	4.0 g
Brightening agent (UVITEX-CK of Ciba-Geigy A.G.)	1.5 g
Water to make	1000 ml
pH (at 25° C)	10.25

Bleach-fixing Solution:	
Water	400 ml
Ammonium thiosulfate (70 wt%)	200 ml
Sodium sulfite	20 g
Ammonium ethylenediaminetetraacetic acid Iron (III)	60 g
Ethylenediaminetetraacetic acid disodium salt	10 g
water to make	1000 ml
pH (at 25° C)	7.00

Rinsing Solution

Ion-exchanged water (Ca, Mg  $\leq$  3 ppm each)

55 Process (III):

Step	Temperature (°C)	Time (sec.)	Amount of Replenisher* (ml)	Tank Capacity (liter)
Color development	35	45	161	17
Bleach-fixing	30 - 36	45	215	17
Stabilizing (1)	30 - 37	20	-	10
Stabilizing (2)	30 - 37	20	-	10
Stabilizing (3)	30 - 37	20	-	10
Stabilizing (4)	30 - 37	30	248	10
Drying	70 - 85	60		

\* Per square meter of the light-sensitive material.

[The four stabilizing tanks were connected in cascade in such a way that the overflowing stabilizing replenisher ran in order from tank (4) to tank (1).]

The processing solutions had the following compositions.

**Color Developer:**

	<b><u>Tank Solution</u></b>	<b><u>Replenisher</u></b>
<b>Water</b>	<b>800 ml</b>	<b>800 ml</b>
<b>Ethylenediaminetetraacetic acid</b>	<b>2.0 g</b>	<b>2.0 g</b>
<b>5,6-Dihydroxybenzene-1,2,4-tri-sulfonic acid</b>	<b>0.3 g</b>	<b>0.3 g</b>
<b>Triethanolamine</b>	<b>8.0 g</b>	<b>8.0 g</b>

	Potassium bromide	0.6 g	-
5	Potassium carbonate	25 g	25 g
	N-Ethyl-N-(8-methanesulfonamidoethyl)- 3-methyl-4-aminoaniline sulfate	5.0 g	7.0 g
10	Diethylhydroxylamine	4.2 g	6.0 g
	Brightening agent (4,4'-diamino- stilbene based compound)	2.0 g	2.5 g
15	Water to make	1000 ml	1000 ml
	pH (at 25°C)	10.05	10.45

Bleach-fixing Solution

(Same for both Tank Solution and Replenisher):

20	Water	400 ml
	Ammonium thiosulfate (70 wt%)	100 ml
25	Sodium sulfite	17 g
	Ammonium Ethylenediaminetetraacetic acid iron (III)	55 g
30	Ethylenediaminetetraacetic acid disodium salt	5 g
	Glacial acetic acid	9 g
35	Water to make	1000 ml
	pH (at 25°C)	5.40

Stabilizing Solution

(Same for both Tank Solution and Replenisher):

	Formaldehyde (37% aq. sol.)	0.1 g
45	Formaldehyde-sulfurous acid adduct	0.7 g
	5-Chloro-2-methyl-4-isothiazolin-3-one	0.02 g
	2-Methyl-4-isothiazolin-3-one	0.01 g
50	Copper sulfate	0.005 g

Water to make

1000 ml

pH (at 25°C)

4.0

Process (IV):

The samples exposed were subjected to running development with Fuji Color Roll Processor FMPP 1000 (partly modified) (by Fuji Photo Film Co.) under the conditions described below.

Step	Time (seconds)	Temperature	Tank Capacity (liter)	Amount of Replenisher (ml/m <sup>2</sup> )
Color Development	45	35 ° C	88	150
Bleach-fixation	45	35 ° C	35	50
Rinsing (1)	20	35 ° C	17	-
Rinsing (2)	20	35 ° C	17	-
Rinsing (3)	20	35 ° C	17	250

The rinsing step was carried out by means of a three tank-countercurrent system, where a replenisher was replenished into the rinsing tank (3), the solution overflow from the rinsing tank (3) was introduced into the bottom of the rinsing tank (2), the solution overflow from the rinsing tank (2) was introduced into the bottom of the rinsing tank (1), and the solution overflow from the rinsing tank (1) was drained out therefrom. The amount of the processing solution as taken out from the previous bath into the next bath together with the photographic paper being processed in this system was 25 ml pr m<sup>2</sup> of the paper.

The processing solutions in the respective tanks and the replenishers had the following compositions:



<u>Color Developer:</u>		<u>Tank</u> <u>Solution</u>	<u>Replenisher</u>
5	Water	800 ml	1000 ml
	Diethylenetriamine-pentaacetic acid	3.0 g	3.0 g
10	Benzyl alcohol	15 ml	17 ml
	Diethylene glycol	10 ml	10 ml
	Sodium sulfite	2.0 g	2.5 g
15	Potassium bromide	0.5 g	-
	Sodium carbonate	30 g	35 g
20	N-Ethyl-N-( $\beta$ -methanesulfonamido-ethyl)-3-methyl-4-aminoaniline-sulfate	5.0 g	7.0 g
	Hydroxylamine sulfate	4.0 g	4.5 g
25	Brightening agent	1.0 g	1.5 g
	Water to make	1000 ml	1000 ml
30	pH	10.10	10.50
<u>Bleaching-fixation Solution:</u>		<u>Tank</u> <u>Solution</u>	<u>Replenisher</u>
35	Water	400 ml	400 ml
	Ammonium thiosulfate (70 wt%)	150 ml	300 ml
	Sodium sulfite	12 g	25 g
40	Ammonium ethylenediamine-tetraacetic acid iron (III)	55 g	110 g

	2Na Ethylenediamine-tetraacetate	5 g	10 g
5	Water to make	1000 ml	1000 ml
	pH (25°C)	6.70	6.50

**Rinsing Solution**

10	Ethylenediamine-N,N,N',N'-tetramethylene-phosphonate	0.3 g
	Benzotriazole	1.0 g
15	Water to make	1000 ml
	Sodium hydroxide to make	pH 7.5

Process (V):

Step	Time	Temperature	Tank Capacity (liter)	Amount of Replenisher (ml/m <sup>2</sup> )
Color Development	45 sec	35°C	88	150
Bleach-fixation	2 min	35°C	35	350
30 Rinsing (1)	1 min	35°C	17	-
Rinsing (2)	1 min	35°C	17	-
Rinsing (3)	1 min	35°C	17	1300

The processing solutions and the replenishers were same as those used in the process (IV).

**EXAMPLE 14**

Additional samples were prepared as in Example 12 except that the silver halide emulsions (EM-1 to EM-6) employed in the light-sensitive materials prepared in Example 12 were respectively replaced by silver halide emulsions (EM-7 to EM-12) characterized below, or that couplers ExC-1 to ExC-6 were used as cyan couplers.

Emulsion	Grain Morphology	Grain Size (μm)	Cl Content (mol%)	Coefficient of Variation	Sensitizer Dye
45 EM-7	cubic	1.1	99.0	0.1	(ExS-4)
EM-8	cubic	0.8	99.0	0.1	(ExS-4)
EM-9	cubic	0.45	98.5	0.09	(ExS-3, 5)
EM-10	cubic	0.34	98.5	0.09	(ExS-3, 5)
50 EM-11	cubic	0.45	98.5	0.09	(ExS-8, 12)
EM-12	cubic	0.34	98.4	0.10	(ExS-8, 12)

The performance of the samples was evaluated as in Example 12 and the compounds used in the present invention proved to be equally effective in preventing the occurrence of stains in magenta image irrespective of variations in emulsions or couplers in layers other than magenta-forming layers.

The effect of the present invention is apparent from the above description, which is summarized as follows: using the compounds capable of forming a chemically inactive and substantially colorless compound by forming a chemical bond with an aromatic amine series color developing agent that remains in

the photographic materials after being processed for color development, the deterioration of the image quality of the color photographs prepared and the generation of stains in the photographs, which would occur after being stored for a long period of time, can effectively be prevented. This effect can sufficiently be attained even when the photographic materials are processed with processing solutions from which a noticeable amount of components of the processing solutions would enter into or adhere onto the photographic materials processed, such as processing solutions under running state, rinsing solutions containing a small amount of water or water-free rinsing solutions, substantially benzyl alcohol-free color developers or when the photographic materials are processed with other processing solutions which would be a burden on color development.

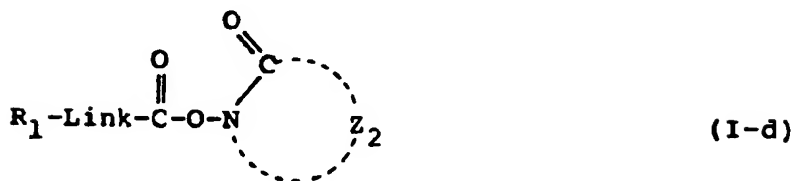
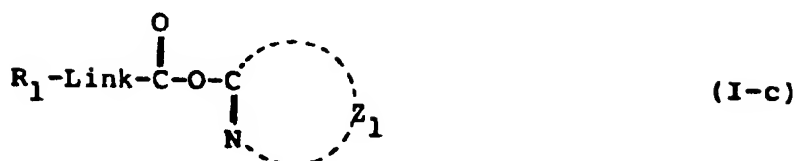
# Claims

1. A color photograph containing a storability-improving compound capable of forming a chemical bond with an aromatic amine series color developing agent that remains in a photographic material after having been processed for color development, under the condition of a pH of 8 or less to give a chemically inactive and substantially colorless compound in at least one photographic layer on a support, characterized in that the storability-improving compound is selected from compounds of general formula (I) and (II):



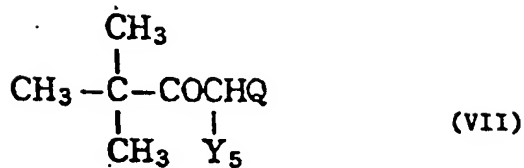
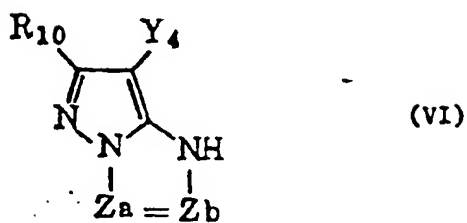
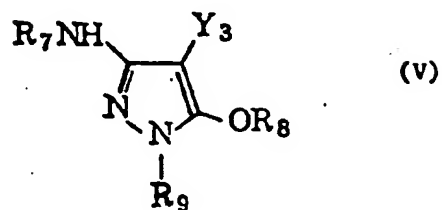
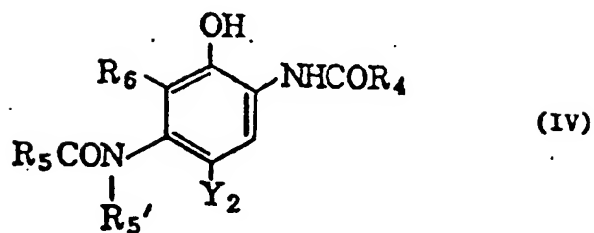
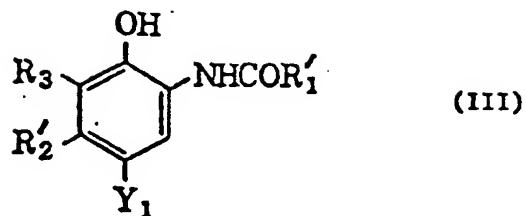
in which  $R_1$  and  $R_2$  each represents an aliphatic group, an aromatic group or a heterocyclic group;  $X$  represents a group capable of reacting with an aromatic amine developing agent to be removed;  $A$  represents a group capable of reacting with an aromatic amine developing agent to form a chemical bond;  $n$  represents 1 or 0;  $B$  represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group or a sulfonyl group;  $Y$  represents a group capable of accelerating the addition of an aromatic amine developing agent to the compound of the formula (II); and  $R_1$  and  $X$ , and  $Y$  and  $R_2$  or  $B$  may be bonded together to form a cyclic structure.

2. A color photograph as claimed in claim 1, wherein the storability-improving compound has a secondary reaction rate constant  $k_2$  (80°C) with p-anisidine in the range of from 1.0 liter/mol\*sec to  $1 \times 10^{-5}$  liter/mol\*sec.
3. A color photograph as claimed in claim 2, wherein the storability-improving compound has a secondary reaction rate constant  $k_2$  (80°C) with p-anisidine or from  $1 \times 10^{-1}$  liter/mol\*sec to  $1 \times 10^{-4}$  liter/mol\*sec.
4. A color photograph as claimed in claim 1, wherein the compound of formula (I) is selected from compounds of general formulae (I-a), (I-b), (I-c) and (I-d) and has a secondary reaction rate constant  $k_2$  (80°C) with p-anisidine in the range of from  $1 \times 10^{-1}$  liter/mol\*sec to  $1 \times 10^{-5}$  liter/mol\*sec.



where  $R_1$  has the same meaning as  $R_1$  in formula (I); Link is a single bond or -O-; Ar denotes an aromatic group having the same meaning as defined for  $R_1$ ,  $R_2$  and B, except that no group useful as a photographic reducing agent such as a hydroquinone derivative or a catechol derivative is released as a result of reaction with an aromatic amine series developing agent; Ra, Rb and Rc, which may be the same or different, each represents a hydrogen atom, or an aliphatic group, an aromatic group or a heterocyclic group having the same meaning as defined for  $R_1$ ,  $R_2$  and B; Ra, Rb and Rc may further represent an alkoxy group, an aryloxy group, a heterocyclic oxy group, an alkylthio group, an arylthio group, a heterocyclic thio group, an amino group, an alkylamino group, an acyl group, an amino group, a sulfonamido group, a sulfonyl group, an alkoxycarbonyl group, a sulfo group, a carboxyl group, a hydroxyl group, an acyloxy group, a ureido group, a urethane group, a carbamoyl group or a sulfamoyl group, provided that Ra and Rb, or Rb and Rc, may combine to form a 5- to 7-membered hetero ring, which hetero ring may be further substituted by a substituent, or form a spiro ring, a bicyclo ring, or may be fused with an aromatic ring;  $Z_1$  and  $Z_2$  denote the non-metallic atomic group necessary for forming a 5- to 7-membered hetero ring, which hetero ring may be further substituted by a substituent, or form a spiro ring, a bicyclo ring, or may be fused with an aromatic ring, except that  $Z_1$  is not such a group that it releases a coupler, a 11-phenyl-3-pyrazolide as a result of reaction with an aromatic amine series developing agent.

5. A color photograph as claimed in claim 4, wherein the compound of formula (I) contained in the photographic material contains compound of general formula (I-a) or (I-b) having the total number of at least 13 carbon atoms.
6. A color photograph as claimed in claim 1, wherein the photographic layer contains the storability-improving compound together with a yellow coupler, a magenta coupler or a cyan coupler.
7. A color photograph as claimed in claim 6, wherein the coupler is selected from compounds of general formulae (III), (IV), (V), (VI) and (VII):

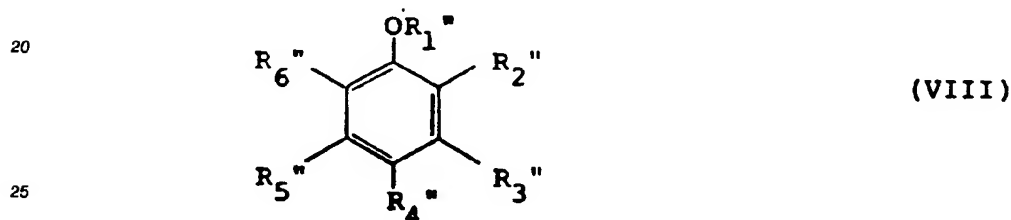


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in which R'1, R4 and R5 each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R'2 represents an aliphatic group; R3 and R6 each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic-oxy group or an

acylamino group;  $R_5'$  represents a hydrogen atom or has the same meaning as  $R_5$ ;  $R_7$  and  $R_9$  each represents a substituted or unsubstituted phenyl group;  $R_8$  represents a hydrogen atom, an aliphatic or aromatic acyl group or an aliphatic or aromatic sulfonyl group;  $R_{10}$  represents a hydrogen atom or a substituent; Q represents a substituted or unsubstituted N-phenylcarbamoyl group;  $Za$  and  $Zb$  each represents a methine group, a substituted methine group or  $=N-$ ;  $Y_1$ ,  $Y_2$ ,  $Y_3$ ,  $Y_4$  and  $Y_5$  each represents a hydrogen atom or a group capable of being removed in coupling reaction with an oxidized product of a developing agent;  $R_2'$  and  $R_3$ , and  $R_5$  and  $R_6$  each may form a 5-, 6- or 7-membered ring;  $R_1'$ ,  $R_2$ ,  $R_3$  or  $Y_1$ ;  $R_4$ ,  $R_5$ ,  $R_6$ , or  $Y_2$ ;  $R_7$ ,  $R_8$ ,  $R_9$ , or  $Y_3$ ;  $R_{10}$ ,  $Za$ ,  $Zb$  or  $Y_4$ ; and Q or  $Y_5$  each may form a dimer or a higher polymer.

8. A color photograph as claimed in claim 1, wherein the photographic layer further contains an anti-fading agent together with the storability-improving agent.
9. A color photograph as claimed in claim 8, wherein the anti-fading agent is an aromatic compound of a general formula (VIII):

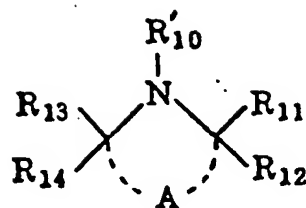


wherein  $R_1''$  represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group or a group of



where  $R_7''$ ,  $R_8''$  and  $R_9''$  may be the same or different and each represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an alkenoxy group or an aryloxy group;  $R_2''$ ,  $R_3''$ ,  $R_4''$ ,  $R_5''$  and  $R_6''$  may be the same or different and each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acylamino group, an alkylamino group, an alkylthio group, an arylthio group, an alkoxy carbonyl group, an aryloxy carbonyl group, a halogen atom or  $-OR_1''$ , where  $R_1''$  has the same meaning as  $R_1'$ ; or  $R_1''$  and  $R_2''$  may be bonded together to form a 5-membered ring, a 6-membered ring or a spiro ring; or  $R_2''$  and  $R_3''$ , or  $R_3''$  and  $R_4''$  may be bonded together to form a 5-membered ring, a 6-membered ring or a spiro ring.

10. A color photograph as claimed in claim 9, wherein the amount of the compound of formula (VIII) to be added is from 10 to 400 mol% to the coupler.
11. A color photograph as claimed in claim 9, wherein the amount of the compound of formula (VIII) to be added is from 30 to 300 mol% to the coupler.
12. A color photograph as claimed in claim 8, wherein the anti-fading agent is an amine compound of a general formula (IX):



(IX)

in which R'<sub>10</sub> represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an acyl group, a sulfonyl group, a sulfinyl group, an oxy-radical or a hydroxyl group; R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub> may be the same or different and each represents a hydrogen atom or an alkyl group; and A represents a non-metallic atomic group necessary for forming a 5-membered, 6-membered or 7-membered ring.

13. A color photograph as claimed in claim 12, wherein the amount of the compound of formula (IX) to be added is from 10 to 400 mol% to the coupler.
14. A color photograph as claimed in claim 12, wherein the amount of the compound of formula (IX) to be added is from 30 to 300 mol% to the coupler.
15. A color photograph as claimed in claim 8, wherein the anti-fading agent is a metal complex comprising a center atom of copper, cobalt, nickel, palladium or platinum and at least one organic ligand having two or more conformations.
16. A color photograph as claimed in claim 15, wherein the amount of the metal complex to be added is from 1 to 100 mol% to the coupler.
17. A color photograph as claimed in claim 15, wherein the amount of the metal complex to be added is from 3 to 40 mol% to the coupler.
18. A method for preparation of color photographs wherein a photographic material containing a silver halide emulsion layer and a color image-forming coupler capable of forming a dye by an oxidation-coupling reaction with an aromatic amine series color developing agent, as coated on a support, is imagewise exposed to light and then subjected to photographic processing comprising carrying out photographic processing in the presence of a storability-improving compound capable of forming a chemical bond with the aromatic amine series color developing agent to give a chemically inactive and substantially colorless compound, characterized in that a storability-improving compound as defined in any of claims 1 to 5 is used.
19. The method for preparation of color photographs as claimed in claim 18, wherein the photographic material contains the storability-improving compound in at least one photographic layer.
20. The method for preparation of color photographs as claimed in claim 19, wherein the content of the said storability-improving compound in the photographic material is within the range of from  $1 \times 10^{-2}$  to 10 mols per mol of the color image-forming coupler.
21. The method for preparation of color photographs as claimed in claim 18, wherein said color developer contains benzyl alcohol in an amount of 2.0 ml/liter or less.
22. The method for preparation of color photographs as claimed in claim 18, wherein said color developer contains benzyl alcohol in an amount of 0.5 ml/liter or less.
23. The method for preparation of color photographs as claimed in claim 18, wherein said color developer contains no benzyl alcohol.

24. The method for preparation of color photographs as claimed in claim 18, wherein the color development time is within 2 minutes and 30 seconds or less.
25. The method for preparation of color photographs as claimed in claim 18, wherein the color development time is within the range of from 10 seconds to 2 minutes and 30 seconds or less.
26. The method for preparation of color photographs as claimed in claim 18, wherein the color development time is within the range of from 45 seconds to 2 minutes.

# Revendications

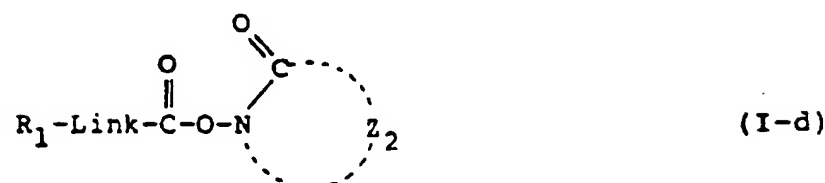
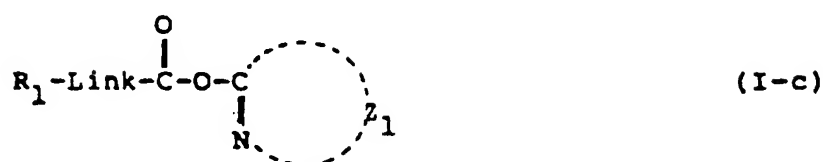
1. Une photographie en couleurs contenant un composé améliorant la stabilité au stockage capable de former une liaison chimique avec un agent développeur chromogène de la série des amines aromatiques qui reste dans un matériau photographique après avoir été traité pour le développement chromogène, à un pH de 8 ou moins pour donner un composé chimiquement inactif et pratiquement incolore dans au moins une couche photographique sur un support, caractérisée en ce que le composé améliorant la stabilité au stockage est choisi parmi les composés de formules générales (I) et (II) :



dans lesquelles  $R_1$  et  $R_2$  représentent chacun un groupe aliphatique, un groupe aromatique ou un groupe hétérocyclique ;  $X$  représente un groupe éliminable par réaction avec un agent développeur du type amine aromatique ;  $A$  représente un groupe capable de réagir avec un agent développeur du type amine aromatique pour former une liaison chimique ;  $n$  représente 0 ou 1 ;  $B$  représente un atome d'hydrogène, un groupe aliphatique, un groupe aromatique, un groupe hétérocyclique, un groupe acyle ou un groupe sulfonyle ;  $Y$  représente un groupe capable d'accélérer l'addition d'un agent développeur du type amine aromatique sur le composé de formule (II) ; et  $R_1$  et  $X$ , et  $Y$  et  $R_2$  ou  $B$  peuvent être reliés ensemble pour former une structure cyclique.

2. Une photographie en couleurs selon la revendication 1, caractérisée en ce que le composé améliorant la stabilité au stockage a une constante de vitesse réaction secondaire  $k_2$  (à 80 °C) avec la p-anisidine dans la gamme de 1,0 l/mol.s à  $1 \times 10^{-5}$  l/mol.s.
3. Une photographie en couleurs selon la revendication 2, caractérisée en ce que le composé améliorant la stabilité au stockage a une constante de vitesse de réaction secondaire  $k_2$  (à 80 °C) avec la p-anisidine de  $1 \times 10^{-1}$  l/mol.s à  $1 \times 10^{-4}$  l/mol.s.
4. Une photographie en couleurs selon la revendication 1, caractérisée en ce que le composé de formule (I) est choisi parmi les composés de formules générales (I-a), (I-b), (I-c) et (I-d) et a une constante de vitesse de réaction secondaire  $k_2$  (à 80 °C) avec la p-anisidine dans la gamme de  $1 \times 10^{-1}$  l/mol.s à  $1 \times 10^{-5}$  l/mol.s.

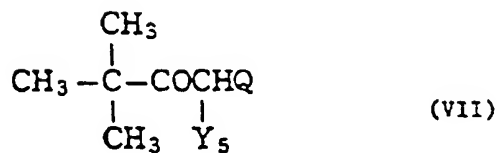
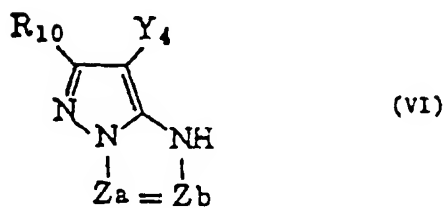
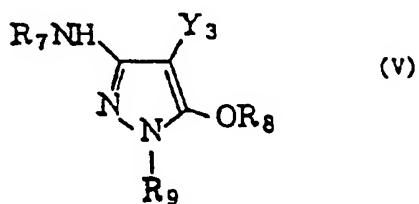
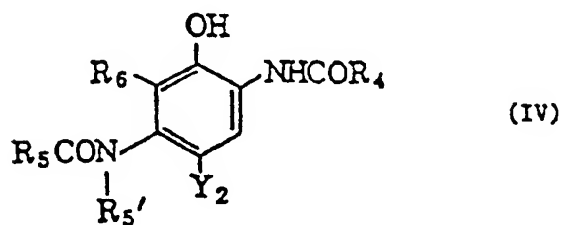
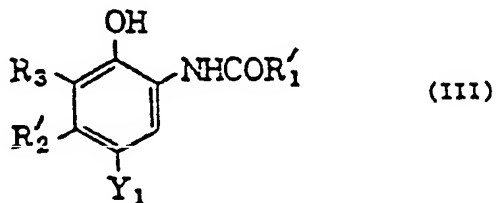




dans lesquelles  $R_1$  a la même définition que  $R_1$  dans la formule (I) ; Link est une liaison simple ou -O- ; Ar représente un groupe aromatique ayant la même signification que pour  $R_1$ ,  $R_2$  et B, sauf que la réaction avec un agent développeur de la série des amines aromatiques ne libère pas de groupe utile comme agent réducteur photographique tel qu'un dérivé d'hydroquinone ou un dérivé de catéchol ; Ra, Rb et Rc, qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène ou un groupe aliphatique, un groupe aromatique ou un groupe hétérocyclique ayant la même signification que pour  $R_1$ ,  $R_2$  et B ; Ra, Rb et Rc peuvent en outre représenter un groupe alcoxy, un groupe aryloxy, un groupe hétérocyclique-oxy, un groupe alkylthio, un groupe arylthio, un groupe hétérocyclique-thio, un groupe amino, un groupe alkylamino, un groupe acyle, un groupe amino, un groupe sulfonamido, un groupe sulfonyle, un groupe alcoxycarbonyle, un groupe sulfo, un groupe carboxyle, un groupe hydroxyle, un groupe acyloxy, un groupe uréido, un groupe uréthane, un groupe carbamoyle ou un groupe sulfamoyle, pourvu que Ra et Rb, ou Rb et Rc, puissent se combiner pour former un hétérocycle à 5-7 chaînons, lequel hétérocycle peut encore être substitué par un substituant ou former un noyau spiranique, un noyau bicyclique, ou puissent être accolés avec un noyau aromatique ;  $Z_1$  et  $Z_2$  représentent le groupe atomique non métallique nécessaire pour former un hétérocyclique à 5-7 chaînons, lequel hétérocyclique peut encore être substitué par un substituant, ou former un noyau spiranique, un noyau bicyclique ou peuvent être accolés avec un noyau aromatique, sauf que  $Z_1$  n'est pas un groupe tel qu'il libère un coupleur, un 1-phényl-3-pyrazolide par réaction avec un agent développeur de la série des amines aromatiques.

5. Une photographie en couleurs selon la revendication 4, caractérisée en ce que le composé de formule (I) contenu dans le matériau photographique contient un composé de formule générale (I-a) ou (I-b) ayant un total d'au moins 13 atomes de carbone.
6. Une photographie en couleurs selon la revendication 1, caractérisée en ce que la couche photographique contient le composé améliorant la stabilité au stockage en même temps qu'un coupleur pour jaune, un coupleur pour magenta ou un coupleur pour cyan.

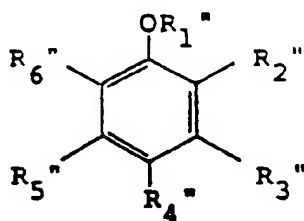
7. Une photographie en couleurs selon la revendication 6, caractérisée en ce que le coupleur est choisi parmi les composés de formules générales (III), (IV), (V), (VI) et (VII) :



dans lesquelles R'1, R4 et R5 représentent chacun un groupe aliphatique, un groupe aromatique, un groupe hétérocyclique, un groupe amino aromatique ou un groupe amino hétérocyclique ; R'2

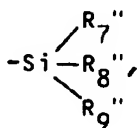
- représente un groupe aliphatique ;  $R_3$  et  $R_6$  représentent chacun un atome d'hydrogène ou d'halogène ou un groupe aliphatique, un groupe aliphatique-oxy ou un groupe acylamino ;  $R_5'$  représente un atome d'hydrogène ou bien il a la même signification que  $R_5$  ;  $R_7$  et  $R_9$  représentent chacun un groupe phényle substitué ou non ;  $R_8$  représente un atome d'hydrogène, un groupe acyle aliphatique ou aromatique ou un groupe sulfonyle aliphatique ou aromatique ;  $R_{10}$  représente un atome d'hydrogène ou un substituant ; Q représente un groupe N-phénylcarbamoyle substitué ou non ; Za et Zb représentent chacun un groupe méthine, un groupe méthine substitué ou =N- ;  $Y_1$ ,  $Y_2$ ,  $Y_3$ ,  $Y_4$  et  $Y_5$  représentent chacun un atome d'hydrogène ou un groupe éliminable dans la réaction de couplage avec un produit d'oxydation d'un agent développeur ;
- $R_2'$  et  $R_3$ , et  $R_5$  et  $R_6$  peuvent former chaque fois un cycle à 5, 6 ou 7 chaînons ;  $R_1'$ ,  $R_2'$ ,  $R_3$  ou  $Y_1$  ;  $R_4$ ,  $R_5$ ,  $R_6$  ou  $Y_2$  ;  $R_7$ ,  $R_8$ ,  $R_9$  ou  $Y_3$  ;  $R_{10}$ , Za, Zb ou  $Y_4$  ; et Q ou  $Y_5$  peuvent chacun former un dimère ou un polymère supérieur.

8. Une photographie en couleurs selon la revendication 1, caractérisée en ce que la couche photographique contient en outre un agent anti-évanouissement en même temps que l'agent améliorant la stabilité au stockage.
9. Une photographie en couleurs selon la revendication 8, caractérisée en ce que l'agent anti-évanouissement est un composé aromatique de formule générale (VIII) :



(VIII)

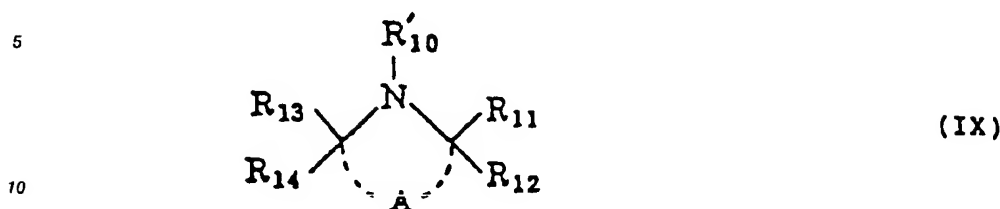
dans laquelle  $R_1''$  représente un atome d'hydrogène, un groupe alkyle, un groupe alcényle, un groupe aryle, un groupe hétérocyclique ou un groupe de formule



- dans laquelle  $R_7''$ ,  $R_8''$ , et  $R_9''$  peuvent être identiques ou différents et représentent chacun un groupe alkyle, un groupe alcényle, un groupe aryle, un groupe alcoxy, un groupe alcényloxy ou un groupe aryloxy ;
- $R_2''$ ,  $R_3''$ ,  $R_4''$ ,  $R_5''$  et  $R_6''$  peuvent être identiques ou différents et représentent chacun un atome d'hydrogène, un groupe alkyle, un groupe alcényle, un groupe aryle, un groupe acylamino, un groupe alkylamino, un groupe alkylthio, un groupe arylthio, un groupe alcoxycarbonyl, un groupe aryloxy-carbonyl, un atome d'halogène ou un groupe -O- $R_1''$ , dans lequel  $R_1''$  a la même signification que  $R_1''$  ; ou bien  $R_1''$  et  $R_2''$  peuvent être reliés ensemble pour former un cycle à 5 ou 6 chaînons ou un noyau spiranique ; ou bien  $R_2''$  et  $R_3''$  ou  $R_3''$  et  $R_4''$  peuvent être reliés ensemble pour former un cycle à 5 ou 6 chaînons ou un noyau spiranique.

10. Une photographie en couleurs selon la revendication 9, caractérisée en ce que la quantité du composé de formule (VIII) à ajouter est de 10 à 400 mol%, par rapport au coupleur.
11. Une photographie en couleurs selon la revendication 9, caractérisée en ce que la quantité de formule (VIII) à ajouter est de 30 à 300 mol% par rapport au coupleur.
12. Une photographie en couleurs selon la revendication 8, caractérisée en ce que l'agent anti-évanouisse-

ment est une amine de formule générale (IX) :



15 dans laquelle R'<sub>10</sub> représente un atome d'hydrogène, un groupe alkyle, un groupe alcényle, un groupe alcynyle, un groupe acyle, un groupe sulfonyle, un groupe sulfinyle, un radical oxyde ou un groupe hydroxyle ; R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> et R<sub>14</sub> peuvent être identiques ou différents et représentent chacun un atome hydrogène ou un groupe alkyle ; et A représente un groupe atomique non métallique nécessaire pour former un cycle à 5, 6 ou 7 chaînons.

- 20 13. Une photographie en couleurs selon la revendication 12, caractérisée en ce que la quantité du composé de formule (IX) à ajouter est de 10 à 400 mol%, par rapport au coupleur.
14. Une photographie en couleurs selon la revendication 12, caractérisée en ce que la quantité du composé de formule (IX) à ajouter est de 30 à 300 mol% par rapport au coupleur.
- 25 15. Une photographie en couleurs selon la revendication 8, caractérisée en ce que l'agent anti-évanouissement est un complexe métallique comprenant un atome central de cuivre, cobalt, nickel, palladium ou platine et au moins un ligand organique ayant deux ou plusieurs configurations.
- 30 16. Une photographie en couleurs selon la revendication 15, caractérisée en ce que la quantité du complexe métallique à ajouter est de 1 à 100 mol% par rapport au coupleur.
17. Une photographie en couleurs selon la revendication 15, caractérisée en ce que la quantité du complexe métallique à ajouter est de 3 à 40 mol% par rapport au coupleur.
- 35 18. Un procédé pour produire des photographies en couleurs dans lequel un matériau photographique contenant une couche d'émulsion d'halogénure d'argent et un coupleur chromogène capable de former un colorant par une réaction d'oxydation-couplage avec un agent développeur chromogène de la série des amines aromatiques, déposée sur un support, est exposé à la lumière suivant une image et ensuite soumis à un traitement photographique consistant à mettre en oeuvre le traitement photographique en présence d'un composé améliorant la stabilité au stockage capable de former une liaison chimique avec l'agent développeur chromogène de la série des amines aromatiques pour donner un composé chimiquement inactif et pratiquement incolore, caractérisé en ce que l'on utilise un composé améliorant la stabilité au stockage selon l'une quelconque des revendications 1 à 5.
- 40 19. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que le matériau photographique contient le composé améliorant la stabilité au stockage dans au moins une couche photographique.
- 45 20. Le procédé pour produire des photographies en couleurs selon la revendication 19, caractérisé en ce que la teneur en ledit composé améliorant la stabilité au stockage dans le matériau photographique est comprise dans la gamme de  $1 \times 10^{-2}$  mol à 10 mol par mole du coupleur chromogène.
- 50 21. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que ledit révélateur chromogène contient de l'alcool benzylique en quantité de 2,0 ml/l ou moins.
- 55 22. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que ledit révélateur chromogène contient de l'alcool benzylique en quantité de 0,5 ml/l ou moins.

23. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que ledit révélateur chromogène ne contient pas d'alcool benzylique.
24. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que la durée de développement chromogène est de 2 min 30 s ou moins.
25. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que la durée de développement chromogène est comprise dans l'intervalle de 10 s à 2 min 30 s.
26. Le procédé pour produire des photographies en couleurs selon la revendication 18, caractérisé en ce que la durée de développement chromogène est comprise dans l'intervalle de 45 s à 2 min.

# Patentansprüche

1. Farbphotographie, enthaltend eine die Lagerfähigkeit verbessernde Verbindung, die fähig ist, mit einem Farbwentwicklungsmittel der aromatischen Amin-Reihe, das in einem photographischen Material nach dessen Farbwentwicklungsbehandlung zurückbleibt, unter der Bedingung eines pH von 8 oder weniger eine chemische Bindung zu bilden, um in mindestens einer photographischen Schicht auf einem Träger eine chemisch inaktive und im wesentlichen farblose Verbindung zu ergeben, dadurch gekennzeichnet, daß die die Lagerfähigkeit verbessernde Verbindung aus Verbindungen der allgemeinen Formel (I) und (II) gewählt ist:



worin bedeuten:

R<sub>1</sub> und R<sub>2</sub> jeweils eine aliphatische Gruppe, aromatische Gruppe oder heterocyclische Gruppe;

X eine Gruppe, die fähig ist, mit einem zu entfernenden aromatischen Amin-Entwicklungsmittel zu reagieren;

A eine Gruppe, die fähig ist, mit einem aromatischen Amin-Entwicklungsmittel zur Bildung einer chemischen Bindung zu reagieren;

n 1 oder 0;

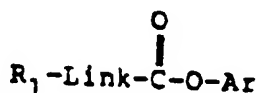
B ein Wasserstoffatom, eine aliphatische Gruppe, aromatische Gruppe, heterocyclische Gruppe, Acylgruppe oder Sulfonylgruppe;

Y eine Gruppe, die fähig ist, die Addition eines aromatischen Amin-Entwicklungsmittels an die Verbindung der Formel (II) zu beschleunigen;

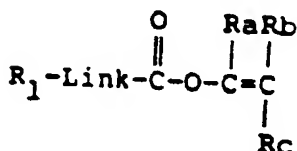
wobei R<sub>1</sub> und X, und Y und R<sub>2</sub> oder B zur Bildung einer cyclischen Struktur miteinander verbunden sein können.

2. Farbphotographie nach Anspruch 1, wobei die die Lagerfähigkeit verbessernde Verbindung eine sekundäre Reaktionsgeschwindigkeitskonstante k<sub>2</sub> (80° C) mit p-Anisidin im Bereich von 1,0 Liter/Mol . sec bis 1 x 10<sup>-5</sup> Liter/Mol . sec besitzt.
3. Farbphotographie nach Anspruch 2, wobei die die Lagerfähigkeit verbessernde Verbindung eine sekundäre Reaktionsgeschwindigkeitskonstante k<sub>2</sub> (80° C) mit p-Anisidin von 1 x 10<sup>-1</sup> Liter/Mol . sec bis 1 x 10<sup>-4</sup> Liter/Mol . sec besitzt.
4. Farbphotographie nach Anspruch 1, wobei die Verbindung der Formel (I) aus Verbindungen der

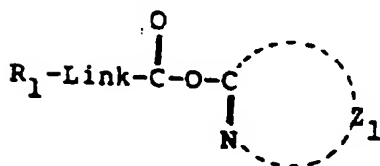
allgemeinen Formeln (I-a), (I-b), (I-c) und (I-d) gewählt ist und eine sekundäre Reaktionsgeschwindigkeitskonstante  $k_2$  (80° C) mit p-Anisidin im Bereich von  $1 \times 10^{-1}$  Liter/Mol . sec bis  $1 \times 10^{-5}$  Liter/Mol . sec besitzt.



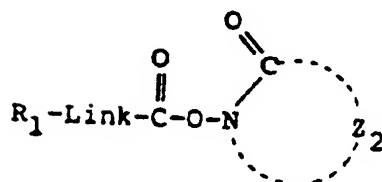
(I-a)



(I-b)



(I-c)



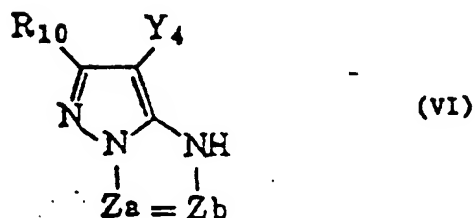
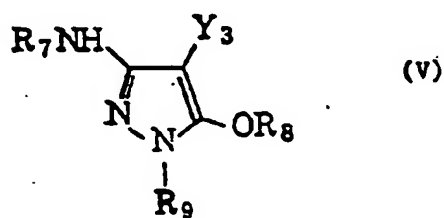
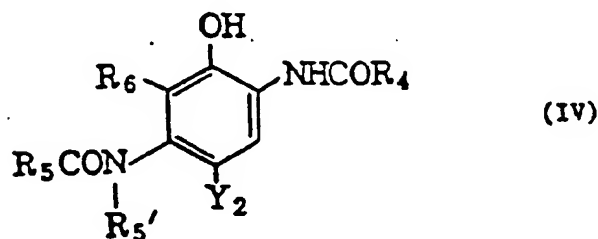
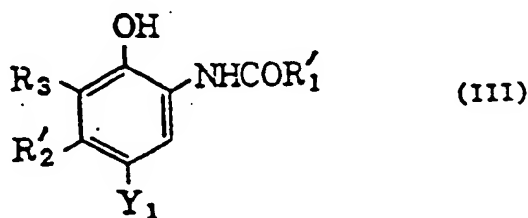
(I-d)

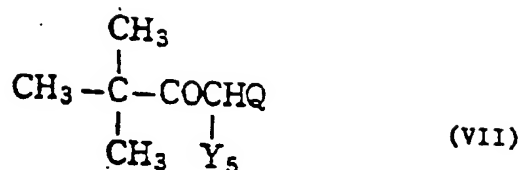
worin  $R_1$  die gleiche Bedeutung wie  $R_1$  in Formel (I) hat; Link eine einfache Bindung oder -O- ist; Ar eine aromatische Gruppe bezeichnet mit der gleichen Bedeutung, wie für  $R_1$ ,  $R_2$  und B definiert, mit der Ausnahme, daß keine als photographisches Reduktionsmittel, wie ein Hydrochinon-Derivat oder ein Catechol-Derivat, geeignete Gruppe als Ergebnis der Reaktion mit einem Entwicklungsmittel der aromatischen Amin-Reihe freigesetzt wird; Ra, Rb und Rc, die gleich oder verschieden sein können, jeweils ein Wasserstoffatom oder eine aliphatische Gruppe, aromatische Gruppe oder heterocyclische Gruppe mit der gleichen Bedeutung, wie für  $R_1$ ,  $R_2$  und B definiert, darstellen; Ra, Rb und Rc können weiterhin eine Alkoxygruppe, Aryloxygruppe, heterocyclische Oxygruppe, Alkylthiogruppe, Arylthiogruppe, heterocyclische Thiogruppe, Aminogruppe, Alkylaminogruppe, Acylgruppe, Aminogruppe, Sulfonamidogruppe, Sulfonylgruppe, Alkoxy-carbonylgruppe, Sulfogruppe, Carboxylgruppe, Hydroxylgruppe, Acyloxygruppe, Ureidogruppe, Urethangruppe, Carbamoylgruppe oder Sulfamoylgruppe bedeuten, mit der Maßgabe, daß Ra und Rb oder Rb und Rc zur Bildung eines 5- bis 7-gliedrigen Heterorings kombiniert sein können, wobei der Heteroring weiterhin durch einen Substituenten substituiert sein kann, oder einen Spiroring, einen Bicycloring bilden können oder mit einem aromatischen Ring kondensiert sein können;  $Z_1$  und  $Z_2$ , die zur Bildung eines 5- bis 7-gliedrigen Heterorings erforderliche nichtmetallische Atomgruppe bedeuten, wobei der Heteroring weiterhin durch einen Substituenten substituiert sein kann, oder einen Spiroring, einen Bicycloring bilden oder mit einem aromatischen Ring kondensiert sein können, mit der Ausnahme, daß  $Z_1$  nicht eine solche Gruppe ist, daß sie einen Kuppler, ein 1-Phenyl-3-pyrazolid als Ergebnis der Reaktion mit einem Entwicklungsmittel der aromatischen Aminreihe freisetzt.

5. Farbphotographie nach Anspruch 4, wobei die in dem photographischen Material enthaltene Verbin-

ung der Formel (I) eine Verbindung der allgemeinen Formel (I-a) oder (I-b) mit einer Gesamtzahl von mindestens 13 Kohlenstoffatomen enthält.

6. Farbphotographie nach Anspruch 1, wobei die photographische Schicht die die Lagerfähigkeit verbessernde Verbindung zusammen mit einem Gelbkuppler, einem Magenta-Kuppler oder einem Cyankuppler enthält.
7. Farbphotographie nach Anspruch 6, wobei der Kuppler aus Verbindungen der allgemeinen Formeln (III), (IV), (V), (VI) und (VII) gewählt ist:





worin bedeuten:

R<sub>1</sub>, R<sub>4</sub> und R<sub>5</sub> jeweils eine aliphatische Gruppe, aromatische Gruppe, heterocyclische Gruppe, aromatische Aminogruppe oder heterocyclische Aminogruppe;

R<sub>2</sub> eine aliphatische Gruppe;

R<sub>3</sub> und R<sub>6</sub> jeweils ein Wasserstoffatom, Halogenatom, eine aliphatische Gruppe, aliphatische Oxygruppe oder Acylaminogruppe;

R<sub>5</sub> ein Wasserstoffatom oder die gleiche Bedeutung wie R<sub>6</sub>;

R<sub>7</sub> und R<sub>9</sub> jeweils eine substituierte oder unsubstituierte Phenylgruppe;

R<sub>8</sub> ein Wasserstoffatom, eine aliphatische oder aromatische Acylgruppe oder eine aliphatische oder aromatische Sulfonylgruppe;

R<sub>10</sub> ein Wasserstoffatom oder einen Substituenten;

Q eine substituierte oder unsubstituierte N-Phenylcarbamoylgruppe;

Za und Zb jeweils eine Methingruppe, substituierte Methingruppe oder =N-;

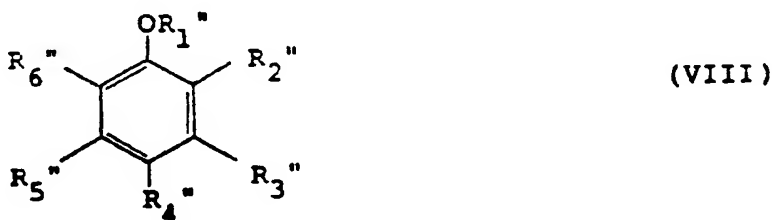
Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub>, Y<sub>4</sub> und Y<sub>5</sub> jeweils ein Wasserstoffatom oder eine Gruppe, die bei der Kupplungsreaktion mit einem oxidierten Produkt eines Entwicklungsmittels entfernt werden kann;

wobei R<sub>2</sub>, R<sub>3</sub> und R<sub>5</sub> und R<sub>6</sub> jeweils einen 5-, 6- oder 7-gliedrigen Ring bilden können;

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> oder Y<sub>1</sub>; R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> oder Y<sub>2</sub>; R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> oder Y<sub>3</sub>; R<sub>10</sub>, Za, Zb oder Y<sub>4</sub>; und Q oder Y<sub>5</sub> jeweils ein Dimer oder ein höheres Polymer bilden können.

8. Farbphotographie nach Anspruch 1, wobei die photographische Schicht weiterhin ein die Verblassung verhinderndes Mittel zusammen mit dem die Lagerfähigkeit verbessernden Mittel enthält.

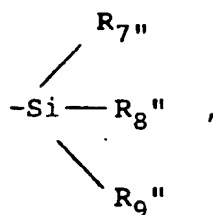
9. Farbphotographie nach Anspruch 8, wobei das die Verblassung verhindernde Mittel eine aromatische Verbindung der allgemeinen Formel (VIII) ist:



worin bedeuten:

R<sub>1</sub>'' ein Wasserstoffatom, eine Alkylgruppe, Alkenylgruppe, Arylgruppe, heterocyclische Gruppe oder eine Gruppe



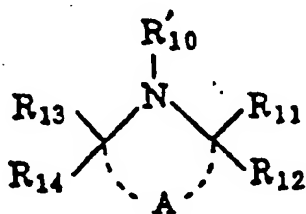


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worin  $R_7''$ ,  $R_8''$  und  $R_9''$  gleich oder verschieden sein können und jeweils eine Alkylgruppe, Alkenylgruppe, Arylgruppe, Alkoxygruppe, Alkenoxygruppe oder Aryloxygruppe bedeuten;  
 $R_2''$ ,  $R_3''$ ,  $R_4''$ ,  $R_5''$  und  $R_6''$ , die gleich oder verschieden sein können, jeweils ein Wasserstoffatom, eine Alkylgruppe, Alkenylgruppe, Arylgruppe, Acylaminogruppe, Alkylaminogruppe, Alkylthiogruppe, Arylthiogruppe, Alkoxy-carbonylgruppe, Aryloxy-carbonylgruppe, ein Halogenatom oder  $-O-R_1'''$ , worin  $R_1'''$  die gleiche Bedeutung wie  $R_1''$  hat;  
 oder  $R_1''$  und  $R_2''$  können zur Bildung eines 5-gliedrigen, 6-gliedrigen oder eines Spirorings miteinander verbunden sein;  
 oder  $R_2''$  und  $R_3''$ , oder  $R_3''$  und  $R_4''$  können zur Bildung eines 5-gliedrigen Rings, eines 6-gliedrigen Rings oder eines Spirorings miteinander verbunden sein.

10. Farbphotographie nach Anspruch 9, wobei die Menge der zuzugebenden Verbindung der Formel (VIII) 10 bis 400 Mol-% bezüglich des Kupplers beträgt.  
 25 11. Farbphotographie nach Anspruch 9, wobei die Menge der zuzugebenden Verbindung der Formel (VIII) 30 bis 300 Mol-% bezüglich des Kupplers beträgt.  
 12. Farbphotographie nach Anspruch 8, wobei das die Verblässung verhindernde Mittel eine Aminverbindung der allgemeinen Formel (IX) ist:

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(IX)

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worin bedeuten:  
 $R_{10}'$  ein Wasserstoffatom, eine Alkylgruppe, Alkenylgruppe, Alkylgruppe, Acylgruppe, Sulfonylgruppe, Sulfonylegruppe, einen Oxyrest oder eine Hydroxylgruppe;  
 $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  und  $R_{14}$ , die gleich oder verschieden sein können, jeweils ein Wasserstoffatom oder eine Alkylgruppe;  
 A eine zur Bildung eines 5-gliedrigen, 6-gliedrigen oder 7-gliedrigen Rings erforderliche nichtmetallische Atomgruppe.

13. Farbphotographie nach Anspruch 12, wobei die Menge der zuzugebenden Verbindung der Formel (IX) 10 bis 400 Mol-% bezüglich des Kupplers beträgt.  
 14. Farbphotographie nach Anspruch 12, wobei die Menge der zuzugebenden Verbindung der Formel (IX) 30 bis 300 Mol-% bezüglich des Kupplers beträgt.  
 55 15. Farbphotographie nach Anspruch 8, wobei das die Verblässung verhindernde Mittel ein Metallkomplex ist, umfassend ein Zentrumsatom aus Kupfer, Kobalt, Nickel, Palladium oder Platin und mindestens einen organischen Liganden mit zwei oder mehreren Konformationen.

16. Farbphotographie nach Anspruch 15, wobei die Menge des zuzugebenden Metallkomplexes 1 bis 100 Mol-% bezüglich des Kupplers beträgt.
- 5 17. Farbphotographie nach Anspruch 15, wobei die Menge des zuzugebenden Metallkomplexes 3 bis 40 Mol-% bezüglich des Kupplers beträgt.
- 10 18. Verfahren zur Herstellung von Farbphotographien, wobei ein photographisches Material, enthaltend eine Silberhalogenidemulsionsschicht und einen farbbildbildenden Kuppler, der fähig ist, durch eine Oxidations-Kupplungsreaktion mit einem Farbentwicklungsmittel der aromatischen Amin-Reihe einen Farbstoff zu bilden, beschichtet auf einem Träger, bildmäßig belichtet und dann einer photographischen Verarbeitung unterzogen wird, umfassend das Ausführen der photographischen Verarbeitung in Gegenwart einer die Lagerfähigkeit verbessernden Verbindung, die fähig ist, mit dem Farbentwicklungsmittel der aromatischen Amin-Reihe eine chemische Bindung zu bilden, um eine chemisch inaktive und im wesentlichen farblose Verbindung zu ergeben, dadurch gekennzeichnet, daß eine die Lagerfähigkeit verbessernde Verbindung, wie in mindestens einem der Ansprüche 1 bis 5 definiert, verwendet wird.
- 15 19. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei das photographische Material die die Lagerfähigkeit verbessernde Verbindung in mindestens einer photographischen Schicht enthält.
- 20 20. Verfahren zur Herstellung von Farbphotographien nach Anspruch 19, wobei Gehalt der die Lagerfähigkeit verbessernden Verbindung in dem photographischen Material innerhalb des Bereichs von  $1 \times 10^{-2}$  bis 10 Mol pro Mol des farbbildbildenden Kupplers liegt.
- 25 21. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei der Farbentwickler Benzylalkohol in einer Menge von 2,0 ml/l oder weniger enthält.
22. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei der Farbentwickler Benzylalkohol in einer Menge von 0,5 ml/l oder weniger enthält.
- 30 23. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei der Farbentwickler keinen Benzylalkohol enthält.
24. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei die Farbentwicklungszeit innerhalb 2 Minuten und 30 Sekunden oder weniger liegt.
- 35 25. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei die Farbentwicklungszeit innerhalb des Bereichs von 10 Sekunden bis 2 Minuten und 30 Sekunden oder weniger liegt.
- 40 26. Verfahren zur Herstellung von Farbphotographien nach Anspruch 18, wobei die Farbentwicklungszeit innerhalb des Bereichs von 45 Sekunden bis 2 Minuten liegt.

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